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SYNTHESIS AND CHARACTERIZATION OF NOVEL POLYAMIDES

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Abstract

There has been a growing interest in producing polymers from bio-based resources as alternatives for fossil resources. One of the most common engineering plastics, polyamides, can be produced from monomers of fossil or renewable origin, such as renewable oils and fats The major drawbacks of polyamides include low molecular weight and poor water stability. The aim of this thesis was to synthesize and characterize long aliphatic segment polyamides by using long chain aliphatic dicarboxylic acids as monomers. .A further objective was to synthesize and characterize novel sulphur-containing polyamides. The monomer of sulfur-containing polyamide was prepared from 10-undecenoic acid via thiol-ene addition reaction. All polyamides were synthesised via polycondenzation.

All long aliphatic polyamides were synthesized successfully with high molecular weight ranges from 37 000-54 000 g/mol. Crucial factors necessary for obtaining high-molecular weight polyamides were identified. The water stabilities of novel polyamides were superior to commercial counterparts, while the presence of sulphur within the polyamide chain enhanced chemical resistance measured as reduced solubility in a range of solvents. All prepared polyamides were fully characterized (NMR, DSC, DMA, Tensile Test, and TGA) and the results of these investigations will be discussed within this thesis. The thermal analyses of these polyamides revealed melting points in the range from 128 to 207 ^{o}C which are rather low compared to the commercial polyamides, Nylon 6 or Nylon 6/6, while the thermal degradation temperature was enhanced.

Keywords Polyamides, Polycondensation, Thiol-ene Additional Reactions

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List of Abbreviations

UDA	10-Undecenoic acid
$CHCl_3$	Chloroform
DCM	Dichloromethane
DMA	Dynamic Mechanical Analysis
DMF	Dimethylformamide
DMPA	2,2-Dimethoxy-2-phenylacetophenone
DMSO	Dimethyl Sulfoxide
DP	Degree of Polymerization
DSC	Differential Scanning Calorimetry
EDT	1,2-Ethanedithiol
GPC	Gel Permeation Chromatography
HDMA	Hexamethylenediamine
HFIP	Hexafluoro-2-Propanol
NMR	Nuclear Magnetic Resonance
PA	Polyamide
PDI	Polydispersity Index
SEC	Size Exclusion Chromatography
S-PA	Sulfur-containning Polyamide
SSP	Solid State Polymerization
T_c	Crystallize Transition Temperature
T_d	Degradation Temperature
TFFA	Trifluroacetic Anhydride
T_g	Glass Transistion Temperature
THF	Tetrahydrofuran
T_m	Melting Temperature
UV	Ultra-Violet
XRD	X-ray Powder Diffraction

1. Introduction

The end of fossil fuel-derived resources is drawing nearer. Currently, petroleum and gas serve as the primary energy sources for polymer production. Organic materials formed fossil substances over the course of millions of years. However, in a little over 200 years, fossil fuel resources have been consumed towards near-exhaustion.

This rapid depletion in resources, in conjunction with increased environmental consciousness and consumer demands has put pressure on both the research community and industry to discover and develop greener and more-sustainable alternatives for petrochemical and polymer production. Bio-based raw materials and their derivatives are the most viable and promising candidates in this respect, due to their numerous environmental and sustainability benefits, as well as the broad variety of molecules which can potentially be obtained from these natural sources.

1.1. Polyamides: Applications and Challenges

Most synthetic polymeric materials are derived from petroleum-based derivatives. As long as fossil fuel prices remain relatively low, petroleum-based polymers will continue to have a larger competitive advantage over bio-based synthetic polymers. However, bio-based raw materials have steadily been attracting attention from both manufacturers and consumers for range of applications. The use of bio-based raw materials can significantly contribute to sustainable development, defined as the development meeting the needs of present without compromising the ability of future generations to meet their own needs. Biomass consists of renewable resources such as corn, sugar cane, soybean which are raw feedstock for bio-polymer synthesis production.

One of the most common commercial thermoplastics is polyamide. Production of two of the most common types of polyamide, Nylon 6 and Nylon 6/6, reached to 7.2 million tons in 2014.[1] Polyamides are engineering plastics that have a lot of outstanding characteristics such as high strength, abrasion resistance, good barrier properties and resilience. The primary applications areas of polyamides are in automotive parts, electrical equipment, electronic products and films and coating (Fig. 1). The high tenacity and breaking energy of polyamide yarns make them suitable for filament/yarn applications, such as fishing nets, ropes, and cables. Polyamides are mass produced for various uses, such as conveyor belts, rubber hoses, and tires. Within old-fashioned, bias-belted automotive tires polyamides are used as a reinforcement, while they serve as a multi-layered matrix phase in aircraft tires.

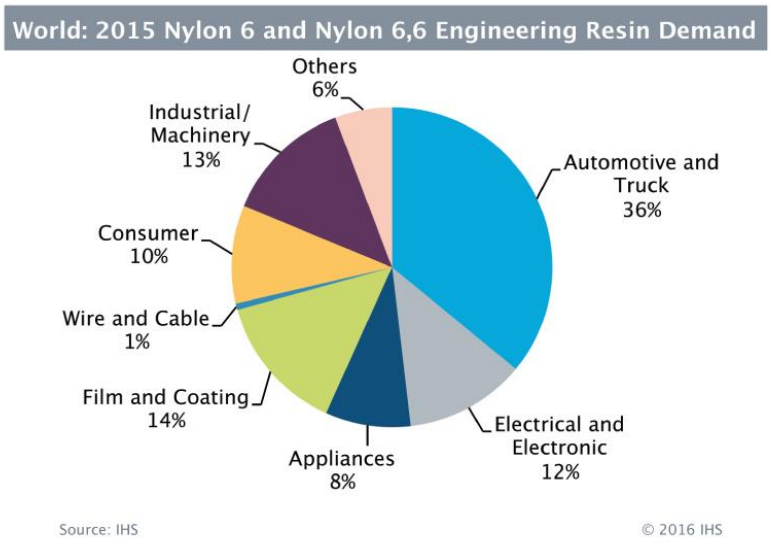


Figure 1. *Nylon and Nylon 6/6 Engineering Resin Demand in 2015*[2]

Besides many excellent properties and a broad range of applications and uses, polyamides still have several disadvantages. Compared with polyolefins such as polypropylene or polyethylene, polyamides have a high degree of moisture absorption, due to its' numerous carbonyl oxygens and amide hydrogens that can readily hydrogen-bond with- and adsorb water molecules. Within polymer networks, waters acts as a plasticizing agent which weakens the secondary bonds between polymer chains, resulting in reduce strength within polyamides. Another feature of commercially-produced polyamides is their relatively low molecular

weight, approximately 10,000-30,000 g/mol. High molecular weight polyamides usually require further processing such as solid-state polymerization which can significantly increase the production cost. At even low molecular weight, the polyamides can provide relative good mechanical properties due to their strong hydrogen bonding between polymer chains.

Therefore, in order to overcome the aforementioned issues and hindrances, the development of novel bio-based, high molecular weight polyamides (and their synthesis and processing techniques) is important to extend the properties and applications of polyamides, while also providing a sustainable yet viable pathway for polymer production.

1.2. Renewable Oils and Fats as Raw Materials for Polyamide Polymerization

Renewable oils and fats are excellent candidates for polymer production. The main constituents of renewable oils and fats are triglycerides of fatty acid (up to 95 wt %), which are amongst the most important resources in the chemical industry.[3] Their variety in composition and ability to be highly-functionalized with an almost limitless range of moieties and functional groups make them suitable as monomers or starting materials for polymer synthesis. There are two main synthesis pathways. One takes advantage of naturally functional groups of triglycerides, such as internal double bonds, epoxides, or hydroxyl groups which can be polymerized using different methods. The second synthesis strategy is chemical modification prior to polymerization. This method overcomes the low reactivity of original triglycerides by introducing easily-polymerizable functional groups. This approach widens the possibility of synthesis pathways and obtainable products.

A wide range of polyamides have been synthesized from fatty acids, such as 11-aminoundecanoic (polyamide 11), sebacic acid (polyamide 6/10, 5/10, 10/10, 4/10). They are both prepared from ricinoleic acid, the major fatty acid component of castor oil. These bio-based polyamides have already been commercialized by

Arkema (France) as specialty polymers under the tradenames Rilsan™[4] (polyamide 11) and Rilsamid™[5] (polyamide 12). Both bio-based polyamides display a vast range of properties, and Rilsan™ exhibits excellent toughness at low temperature and lower moisture absorption compared with Nylon 6 and Nylon 6/6. Moreover, Rilsan™ shows excellent chemical resistance, low density, good thermal, weathering stability and easily processable. Thanks to these outstanding properties, Rilsan™ has a large variety of applications in tubing, hoses for automotive brake and fuel systems, pipes for petroleum and gas industries, food packing, medical and sports equipment.[4]

1.3. Aim and Objectives

1.3.1. Novel Polyamides

The aim of this thesis work was to synthesize, optimize and characterize high molecular weight, long-chain aliphatic polyamides (namely, PA 6/14, 6/16 and 6/18) via polycondensation, utilizing dicarboxylic acids (namely, tetradecanedioic acid (C14), hexadecanedioic acid (C16), octadecanedioic acid (C18)).

The objectives of this thesis included:

- To develop and optimize the complete synthesis pathway for preparing long chain polyamides (from monomer preparation to polycondensation) in laboratory scale
- To determine key conditions and factors within the synthesis process necessary to obtain high molecular weight polyamides with optimal properties
- To characterize the structure, morphological, thermal and mechanical properties of the novel polyamides and compare them against conventional, commercially-available polyamides

1.3.2. Novel Sulphur-Containing Polyamides

Furthermore, an additional aim was to synthesis, characterize and evaluate novel sulphur-containing polyamides prepared from bio-based sources. One castor oil derivative is 10-undecenoic acid, which contains a carboxylic group at one end and an alkene group at the other end of the chain. . The alkene functional group of 10-undecenoic acid can react with a thiol group via a radical thiol-ene (click chemistry) addition reaction, resulting in a thioether linkage. Therefore, two units of 10-undecenoic acid can be coupled with a dithiol, forming a sulfur-containing di-carboxylic acid, which can subsequently be polymerized with diamines via conventional polycondensation.

The thiol-ene addition reaction is classified as a click-chemistry reaction because it's single, high efficiency, conversion and yield reaction. Moreover, the thiol groups can be introduced to the polymer main chains via thiol-ene reactions. According to the Lorentz-Lorenz equation[6,7] the substitution with atoms having high atomic refraction such as sulfur in the polymer chains can increase the refractive index of its polymer. In recent years, the demand for high refractive-index polymers has been increasing dramatically for optical application such as encapsulates for organic light-emitting diode devices, components for charge-coupled devices (CCDs) image sensors (CISs) and so on.[8,9] Therefore, these sulfur-containing polyamides were expected to be novel high performance materials for high-end optical devices.

Part 1

Literature Review

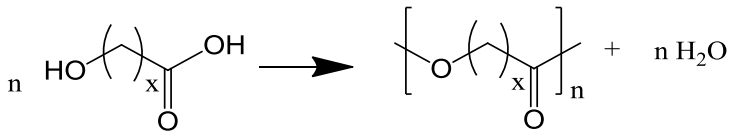
2. Literature Review

2.1. Polycondensation Overview

The classification of polymers can be based on polymer structure or the polymerization mechanism.[10] Polymers are categorized into condensation and addition polymers on the basis of compositional differences between the monomers and their synthesized polymer. Condensation polymer chains were formed by bifunctional or polyfunctional monomers by various condensation reactions of organic chemistry, with the elimination of small molecules such as water or acid chloride. A typical condensation polymer is polyamide synthesized from diamines and diacids with water elimination to form amide linkages.

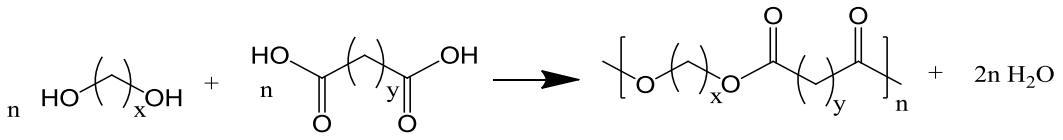
2.1.1. Step Polymerization

Most condensation polymers are produced by step polymerization as mentioned above. Linear condensation polymers are prepared from bifunctional monomers which can have two different functional groups (AB types) or the same functional groups (AABB type). An example of AB type is the step polymerization of carboxylic acids. (Scheme 1)



Scheme 1. *Step Polymerization, AB type.*

The AABB type of step polymerization requires two different initial dimers. This type is demonstrated in Scheme 2 in which diols react to dicarboxylic acids.



Scheme2. *Step Polymerization, AABB type*

2.1.2. Molecular Weight Growth

The molecular weight of condensation polymers increases continuously with the duration of reaction time. In the early stage of polymerization, the molecular weight increases relative slowly due to only oligomers being formed, but when the oligomers combine to produce long chain polymers, the average molecular weight and polymerization degree increase dramatically. Unlike condensation polymerisation, the addition polymer preparation process has initiation, propagation, and termination reaction stages. And a polymer chain's growth only occurs at the propagation step, stopping at termination stage. Therefore, the molecular weight growth of polycondensation only stops when there is no more compatible functional end-groups. This means all polymer chains have the same end-groups which cannot further react with one another.

2.1.3. Reactivity of Functional Groups in Polycondensation

According to the equal reactivity of functional groups assumptions,[10] the reactivity of functional groups in monomers is a constant value which is independent from the size of molecules to which the monomer is attached. This means the reactivity of functional end-groups in monomers, dimers, trimers, polymers are similar. The experimental evidence indicates that the rate constants for esterification in homologous compounds quickly reaches a limiting value, which remains constant and independent of molecular size.[10] Therefore, the reactivity of polycondenszation does not depend on the molecular size.

2.1.4. Kinetics of Polycondensation

The degree of polymerization is a function of reaction time, so the desired molecular weight can be obtained by quenching the reaction at the particular time. Compared with addition-type polymerization, polycondenzation is considered to proceed with relatively slower polymerization rate. Step polymerization is characterized by the disappearance of monomers in the early stage, but long macromolecule chains (approximately more than 5000 g/mol) require a longer reaction time. This is because most of the initial monomers can react either with each other or oligomers in the beginning moment. Hence, for most step polymerizations, there is just small amount of the original monomer (less than 1%) remaining at a point where the average degree of polymerization is approximate to10. Consequently, the polymerization rate is significantly high at the first stage and gradually reduces along the reaction.

2.1.5. Stoichiometric Control

In polycondensation, there are two essential aspects with regard to the control of molecular weight in polymerization, i.e. reaction time and stoichiometric control. Since the properties of the polymer are strongly influenced by their molecular weight, higher or lower molecular weight than desired are equally undesirable. The degree of polymerization is a function of reaction time, after an appropriate time the desired molecular weight can be obtained by terminating the reaction by cooling or exceed monomer addition. In the monomer addition termination method, the polymerization reaction can also be terminated by adjusting the concentration of two monomers; that is, if one of reactants is present in slight excess. The minor reactant will be consumed first, and the excess reactant dominate all the polymer chain's ends. Hence further polymerization is not possible, and the polymer is stable at a particular molecular weight.

The second main factor influencing molecular weight control is stoichiometric balance. In initial stage, an improper stoichiometric balance can lead to a low

molecular weight polymer after a short polymerization time. If there is one kind of monomer even in slight excesses in the beginning of polymerization, the reaction can be terminated quickly. In order to control the stoichiometry, pH monitoring is used to detect the required amount of monomer required to be compensated.

Another important aspect concerning stoichiometric control is the purity of the reactants. If the reactants are contaminated, it can cause undesirable side reactions or inaccurate amount of reactant inputs. The side reactions can influence the rate of polymerization by producing unknown chemicals. Moreover, to keep a polymer's chains growing continuously, the amount of functional groups also must be balanced. The impurities contribute a certain amount towards the total amount of reactants, resulting in one kind of monomer being present in excess.

2.1.6. Mass Transfer Issues[11]

Forcing the polymerization toward the polymer side requires considerable efforts, since the small molecule by-products must diffuse through and out of the reaction mixture. It is difficult to penetrate through when the viscosity of the whole mixture become fairly thick at very high conventions. When the reaction mixture changes from the initial mixture of monomer and oligomers to a high molecular weight polymer, a possible solution is the use of a series of continuous stirred reactors, with different kinds of stirrers. The primary purpose of stirring is assisting the small molecules' volatilization by increasing mass transfer of the molten polymer. Thus, in a polycondensation reactor, the liquid-gas interface is required to circulate continuously and the molten polymer should be spread out as much as possible.

In the final stage of reversible polycondensation, a twin-screw vented extruder is usually used to obtain high molecular weight polymer. The twin-screw vented extruder enhances the interfacial area which assists with the by-products removal. The twin-screw extruders have several advantages such as self-cleaning ability and high shear force which make them a good choice for polyamides and polyurethane.

2.2. Polyamides

According to Research and Markets,[12] the polyamide market is going to reach more than 43 billion US dollars by 2020. The automotive market contributes the biggest share to this market, due to the increased production of lightweight vehicles. Polyamides are utilized in the production of automotive parts, engine covers, air intake manifolds, airbag containers, and various interior or exterior automotive parts. The increase in demand also comes from the production of electronic connectors, semiconductor chips, switches, and other electrical components. Another major sector of polyamide products is fiber applications such as textiles and apparel, carpets, ropes, tire reinforcement, fishing nets, substrates for industrial coated fabrics, etc.

2.2.1. Principles of Polyamides

Polyamides are macromolecules in which repeating units are connected together by amide links. Polyamide is a semi-crystal engineering plastic with high-performance properties, an excellent combination of high strength, flexibility, toughness, abrasion resistance, low coefficient of friction, low creep, chemical resistance, low oxygen permeability, etc. However polyamide also has limitations such as moisture sensitivity and lower resistance to acid hydrolysis than polyester.[10] The moisture sensitivity properties cause changes in dimension and reduce mechanical strength.

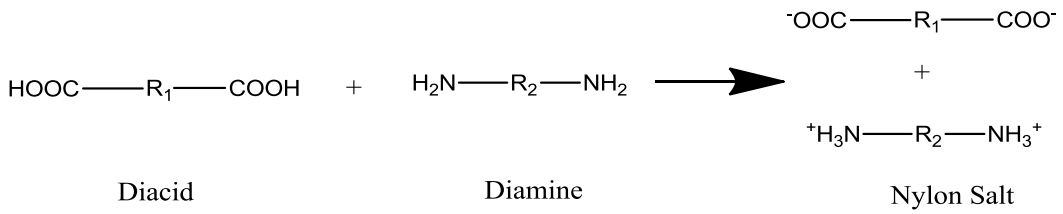
Polyamides are classified into linear aliphatic polyamide (Nylon) and aromatic polyamide known by the commercial name Kevlar®, depending on the monomer(s) type. Nylon 6 and Nylon 6/6 dominate the largest share of the polyamide market. Nylon 6, produced by ring-opening polymerization of ε-caprolactam, market is expected to grow fast, due to the increased demand of Nylon 6 in the production of lightweight vehicles. The amino acid polymerization (AB type) is not appropriate because of the great potential toward cyclization. A typical aromatic polyamide, Kevlar® has similar structure to Nylon 6/6 except that instead of the amide linkages joining by linear hydrocarbons together, they join by benzene rings. Due to low

reactivity of aromatic functional group, compared to aliphatic groups, aromatic polyamides are mainly produced from acid chloride derivatives instead of carboxylic acid as aliphatic polyamides.

2.2.2. Polycondensation for Polyamides[13]

2.2.2.1 Polycondensation for Polyamide 6/6

Unlike Nylon 6, Nylon 6/6 polymerization involves two different monomers, diamine and diacid, which become much more challenging for stoichiometric control. Most AABB polycondensation such as Nylon 6/6 usually involve a Nylon salt preparation step which ensures a 1:1 ratio of diacid and diamine.[14] The product is called a Nylon salt because the reaction is conducted between an acid (dicarboxylic acid) and a base (diamine). The diacid is deprotonated to form cations while the diamine receives protons to become anions according to Brønsted–Lowry[15], acid-base reaction theory (Scheme 3).



Scheme 3. *Nylon salt preparation reaction*

Nylon 6/6 which also is one of the most common commercial polyamides used widely as an engineering thermoplastic. Nylon 6/6 is synthesized from hexamethylenediamine (HMDA) and adipic acid via a polycondensation processes. The commercial production process involves three fundamental steps. In the first step, an approximately equimolar amounts of HMDA and adipic acid are dissolved in an aqueous solution containing 50 wt% water. A particular heat is applied to assist the dissolution process. By monitoring the pH of the nylon salt solution, a particular amount of HMDA is carefully added to compensate of the amount of evaporated HDMA that lost during the polymerization process.

In the second stage, the nylon salt solution is subjected to evaporation at boil. The major amount of water is vapored by boiling at atmospheric pressure. The evaporation process continues until approximate 60-75 w% of monomers and oligomers react with each other. Water evaporation can be conducted using either a batch or a continuous reactor.

Finally, in the third stage, a pressurized vessel is used to remove the rest of water and the polymerization continues with programed conditions that depend on time, position in tubular reactors. In order to avoid precipitating the dissolved nylon salts, a sufficiently high temperature is maintained by keeping high pressure in the reactors. When the polymer chains grow, the water concentration decreases, the pressure can be reduced by controlled ventilation gates to assist the water removal without causing phase separation. Fig. 2 describes the third stage of a continuous production line that produce nylon 6/6 at a high rate in a pressured column reactor.

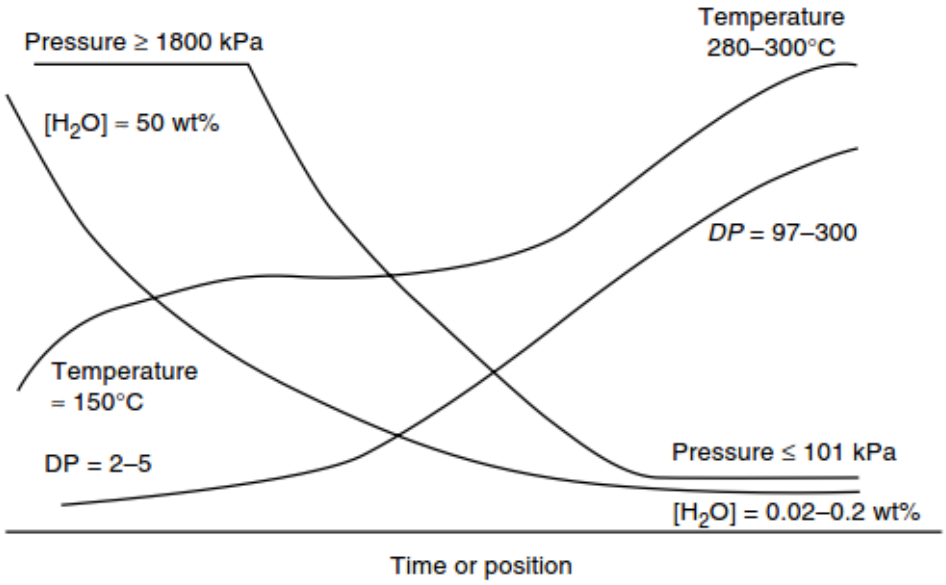


Figure 2. *Process conditions and reaction mixture properties in the course of a typical batch or continuous melt-phase nylon 6/6 polymerization process. Time scale for several hours* [13]

As the high molecular weight polymers is required, the molten nylon can be polymerized further in a high vacuum atmosphere, or sent to a solid-state polymerizer (SSP). In SSP, the reaction temperature approaches the melting point, and the moisture is removed with the assistance of an inner gases purge. The main

advantage of SSP is the low operation temperature where undesirable thermal degradation reactions can be prevented in polymerization. However, the polymer must be re-melted in advance to form filament fibers, which consumes additional energy. An example of an industrial polyester polycondensation reactor is two-stage reactor from AQUAFIL Engineering Company. The schematic of continuous polyester plants was descripted in Fig. 3.

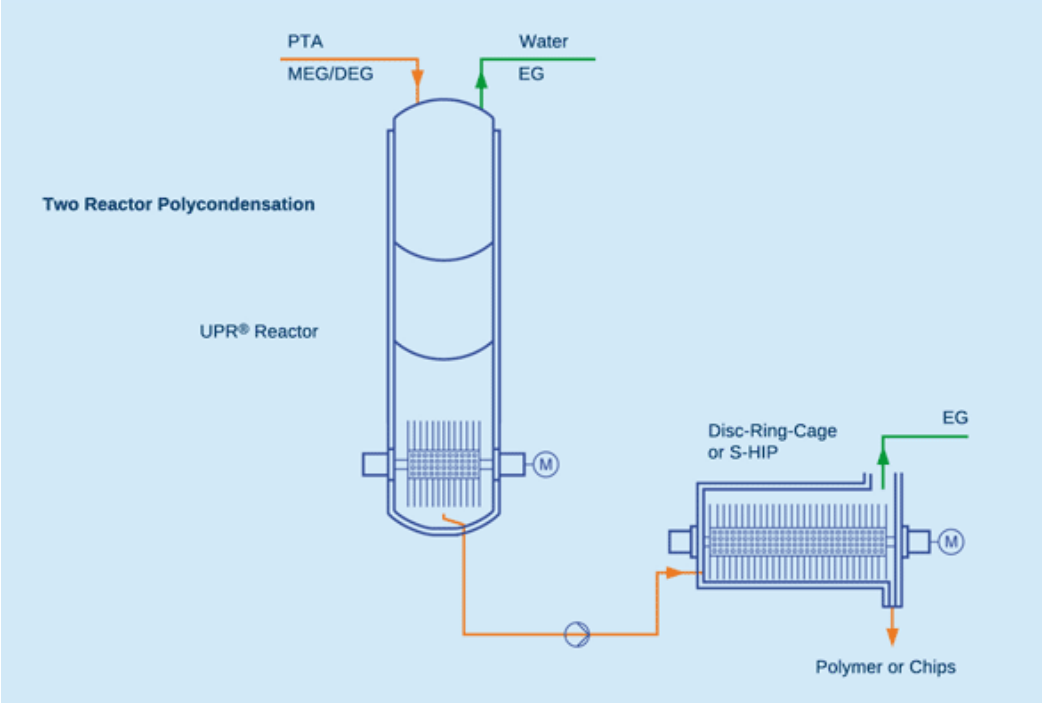


Figure 3. *AQUAFIL ENGINEERING Continuous Polyester Plants*[16]

A remarkable problem of Nylon 6/6 production is thermal degradation. The adipic acid reactant can cyclize to form five-membered rings, leading to the production of cyclopentantone, carbon dioxide and ammonia as gaseous by-products. A trifunctional point on the polymer chains can be created, causing gelation during the polymerization process.

2.2.2.2 Catalysis

Polyamide polymerization can be catalyzed but catalysis is useful in limited circumstances. In most commercial polyamide, the reaction rates are controlled by rate of water removal. There are a number of catalysis are used for polyamidation include metal oxides and carbonates or acidic materials; strong acids; lead

monoxide; terephthalate esters; acid mixtures; and titanium alkoxides or carboxylates.[14] Moreover, the presence of catalyst can also cause reverse reactions during post-manufacture processing. Subsequently, during post-production processing, a catalyzed product can be much more moisture sensitive than an uncatalyzed one.

2.3. Long Aliphatic Segment Polyamides

Nowadays the demand for suitable bio-based materials has increased dramatically due to environmental issues. Both commercial polyamides, Nylon 6 and nylon 6/6 were produced from ε-caprolactam, and adipic acid with hexamethylene diamine, respectively, which are fossil-based materials. Bio-based long-chain polyamides such as PA 4/10 (EcoPaXX®), PA 6/10, PA 10/10, PA 10/12 (Vestamid® Terra) claim to offer outstanding performance with remarkable chemical resistance, low moisture absorption, combined with a very high melting point and high crystallization rate. However, commonly, polyamides with long aliphatic chain tend to decrease stiffness, melting point and specific gravity.

Compared with polyolefins, polyamides have a higher degree of crystallinity which leads to a higher melting point, resulting in processing difficulties. Moreover, thanks to their aliphatic structure, polyolefins such as polyethylene and polypropylene exhibit better chemical resistance than nylon. Therefore, when the backbone of polyamide is tailored with long aliphatic segments, polyamides will become a complementary polymer grade to fill the gap between polyamides and polyolefin. Ehrenstein reported that there was a remarkable improvement in compatibility between polyolefins and polyamides when long aliphatic segment polyamides were used as a compatibilizer.[17]

A series of long aliphatic polyamides (carbon number range from 10 to 34) were reported in literatures by A. C. Boussia[18], X. Cui[19–23], C. Bennett[24,25], F. Pardal[26], Y. Huang[27], W. Li[28], and M. Ehrenstein[17,29,30]. They claimed that increasing the length of aliphatic segment in polyamides will reduce the melting point due to reducing the density of amide groups (Fig. 4). The density of amides has a direct

influence on the melting point because it creates hydrogen bonds between polymer chains. The hydrogen boding resulted from the hydrogens of NH groups interacting with the oxygen of CO groups.

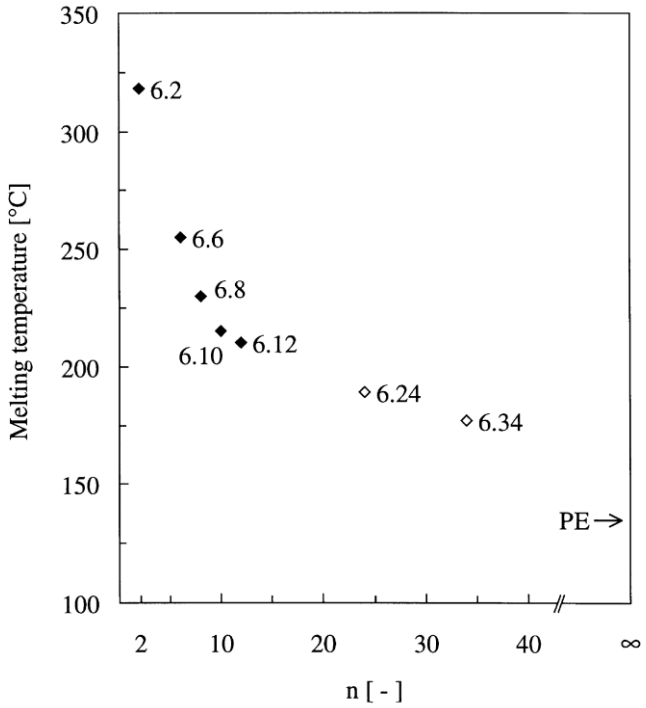


Figure 4. *Melting temperature of polyamide series PA 6/X*[17]

The properties of polyamides are directly related to the nature of repeating units and how they are processed. The degree of crystallinity is obviously influenced by the monomer, but the correlation between the two requires further study.

2.3.1. Polymerization of Long Aliphatic Segments Polyamides

In principle, the synthetic pathway of long aliphatic segments polyamides works in the same way as for common nylons, i.e. condensation polymerization. Polymerizations conducted between diacid and diamine (AABB type) have been the main synthesis pathway for long aliphatic segments of nylon. In the case of the long aliphatic segment, monomers containing both amine and carboxylic groups are not preferred due to their high complexity and difficulty in processing.

A typical melt condensation polymerization process was reported by X. Cui[19–23], M. Ehrestein[17,29,30]. In the case of AABB type polycondensation, the stoichiometry must be controlled precisely to achieve high molecular weight polymers. The imbalance between amine and carboxyl groups can lead to polymerization termination, resulting in low molecular weight polymers. Hence, the nylon salt preparation step is essential in AABB type polycondensation.

2.3.2. Properties of Long Aliphatic Segment Polyamide

2.3.2.1. Molecular Weight

The most valuable practical parameters of polymerization are average molecular weight and molecular weight distribution, because the physical, chemical characteristics are directly influenced by them. Intrinsic viscosity measurement is a relatively simple and fast analysis technique to estimate the average molecular weight of polymer, especially useful in the case of long aliphatic long segment polyamides due to the poor solubility and unknown end groups. The viscosity-average molecular weight is derived from the Mark-Houwink equation (for nylon 6/6)[32]:

$$[\eta] = 0.005 + 3.52 \times 10^{-3} M^{0.551}$$

Gel Permeation Chromatography, light scattering, and NMR analyses were also used to determine the molecular weight of macromolecules. The variation range of molar mass was relative wide due to difference in analysis technique, preparation methods, staring materials, and the nature of repeating unit. Several synthesized polyamides were displayed in Table 1 as references.

As a general issue for all polyamides, their molecular weights are relative low due to difficulty of removing by-product in the final stage of polymerization when their viscosity become significant high. These long aliphatic polyamides also have the same challenge in molecular growth.

Table 1. *Molecular Weight of lab-scale synthesized Polyamides*

Polyamide	**M_n (g/mol)**	**M_w/M_n**
PA 6/34[30]	30 000[a]	
PA 6/12[18]	15 200	
PA 6/13[18]	12 300	
PA 12/18[20]	21 065[b]	1.66
PA 10/18[20]	19 159[b]	1.75
PA 12/16[28]	20 000[a]	
PA 11/12[23]	33 000[a]	
PA 11/10[23]	35 000[a]	
PA 12/11[21]	25 000[a]	
PA 10/11[21]	24 000[a]	
PA 6/20[26]	11 050[c]/ 10 950[d]/ 38 200[b]	
PA 8/18[25]	23 390[a]	

[a] Determined by Intrinsic Viscosity method

[b] Determined by SEC

[c] Determined by ^{1}H NMR

[d] Determined by ^{13}C NMR

2.3.2.2. Thermal Transitions

A summary of the melting points of polyamides is listed in Table 2. As a rule of thumb, it was realized that melting point decreased with an increase in the aliphatic content of both diamine and diacid monomers. This indicates a decrease in the relative concentration of inter-amide hydrogen bonds versus the length of methylene segments. The multi melting peaks were also observed for several polyamides, which is a common phenomenon for semicrystalline polymers.[33] TGA analysis results reveal that all polyamides have high thermal stability with the decomposition temperature above $450^{0}C$.[18,20,21,23–25,28]

Table 2. *Melting points of Polyamides (PA X/Y). X is carbon number of diamine. Y is carbon number of diacid.*

	X					
Y	2	4	6	8	10	12
4	NA	NA	275[34]	254[34]	242[34]	237[34]
6	315[34]	295[34]	265[34]	250[34]	240[34]	229[34]
8	294[34]	253[34]	234[34]	227[34]	222[34]	213[34]
10	280[34]	243[34]	223[34]	210[34]	200[34]	188[34]
12	262[34]	237[34]	215[34]	205[34]	193[34]	181[34]
14	NA	230[35]	**208**[18]	NA	NA	NA
16	235[28]	218[28]	**206**[28]	185[28]	178[28]	170[28]
18	229[25]	218[25]	**197**[25]	185[25]	NA	172[25]
20	230[36]	209[36]	195[36]	184[36]	177[36]	170[36]
22	216[37]	207[37]	189[37]	180[37]	173[37]	170[37]
24	NA	NA	189[17]	NA	NA	NA
34	190[30]	189[30]	177[30]	174[30]	169[30]	166[30]

X is carbon number of diamine. Y is carbon number of diacid.

2.4.2.3. Mechanical Properties

In comparison with common nylons (PA 6, PA 6/6), the mechanical properties of long aliphatic chain polyamides are rather low (Fig. 5 and 6). These polyamides have lower degree of amide groups, therefore the bonding between polymer chains reduced, resulting in decreasing their mechanical properties. The degree of amide groups is a constant value, however the mechanical properties can be improved by enhancing the molecular weight of polyamides.

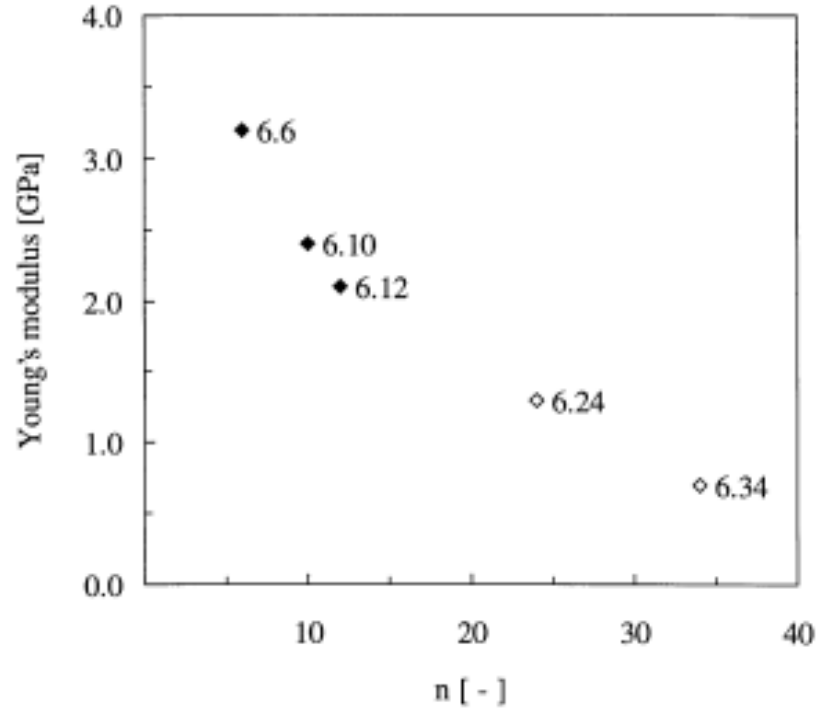


Figure 5. *Young's Modulus of Polyamides (n is carbon number of diamines)*[17]

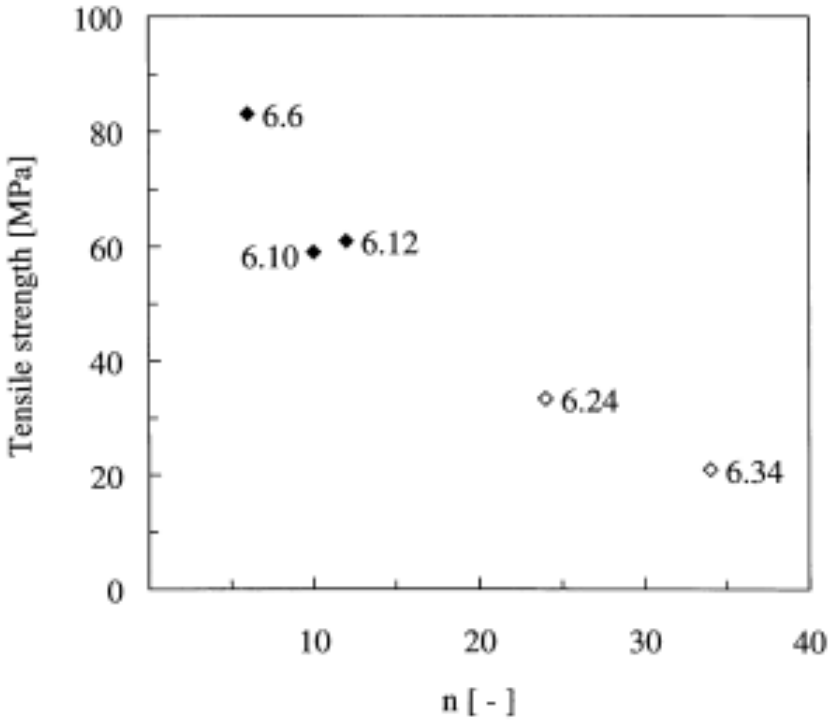


Figure 6. *Tensile Strength of Polyamides (n is carbon number of diamines)*[17]

2.3.2.4. Solubility

The solubility of nylon was examined in a wide range of solvents by M. Ehrenstein[17], X. Cui[20,21], and C. Bennett[24,25]. In general, thanks to its long hydrocarbon segments, long aliphatic nylons did not dissolve in common solvents for nylon such as m-cresol, sulfuric acid,[17] or benzene, toluene, hexane, o-dichlorobenzene, dimethyl sulfoxide, formic acid[24] at ambient atmosphere. There were a few solvents and solvent mixtures at particular ratios which dissolved these polyamides. For NMR analysis, a solvent mixture of trifluoroacetic andhyride and dichloromethane (1:1 v/v ratio) was trusted as an efficient solvent. This mixture was also used for SEC analysis (dichloromethane used as eluent solvent) to dissolve long aliphatic nylon.[26] Besides, formic acid/dichloromethane (1:1 v/v ratio), trifluoethanol/chloroform (8:2 v/v ratio), trifluoacetic acid were also good solvents.[31] An example of solubility of long aliphatic segments polyamides (PA 6/24, PA 6/34) is presented in Table 3 and 4.

Table 3. *Solubility of PA 6/24 and PA 6/34*[17]

Solubility of PA-6.24 and PA-6.34 in various liquids. Key: (−) insoluble, (+) soluble, (G) forms gel

Solvent	PA-6.6		PA-6.24		PA-6.34	
	25°C	50°C	25°C	50°C	25°C	50°C
Toluene	−	−	−	−	−	−
Chloroform	−	−	−	−	−	−
NMP	−	−	−	−	−	−
DMSO	−	−	−	−	−	−
m-Cresol	+	+	−	+	−	+
Formic acid	+	+	−	−	−	−
Sulfuric acid	+	+	+	+	G[a]	G[a]
Methanesulfonic acid	+	+	+	+	+	+
Ethanesulfonic acid	+	+	+	+	+	+

[a] Soluble at 80°C.

Table 4. *Solubility of PA 2/34, PA 4/34, PA 6/34, PA 10/34, and PA 12/34.*[30]

Solvent	PA-6.6		PA-2.34		PA-4.34		PA-6.34		PA-8.34		PA-10.34		PA-12.34	
	25 °C	50 °C	25 °C	50 °C	25 °C	50 °C	25 °C	50 °C	25 °C	50 °C	25 °C	50 °C	25 °C	50 °C
Heptane	–[a]	–	–	–	–	–	–	–	–	–	–	–	–	–
Toluene	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1,2,3,4-Tetrahydronaphthalene	–	–	G[b]	G[b]	G[b]	G[b]	G[b]	G[b]	G[b]	G[b]	G[b]	G[b]	G[b]	G[b]
DMF	–	–	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]
m-Cresol	+	+	–	+	–	+	–	+	–	+	–	+	–	+
Formic acid	+	+	–	–	–	–	–	–	–	–	–	–	–	–
Sulfuric acid	+	+	G[c]	G[c]	G[c]	G[c]	G[c]	G[c]	G[c]	G[c]	G[c]	G[c]	G[c]	G[c]
Methanesulfonic acid	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethanesulfonic acid	+	+	+	+	+	+	+	+	+	+	+	+	+	+

[a] (–) = insoluble, (+) = soluble, (G) = forms gel.
[b] Soluble at around 150 °C.
[c] Soluble at around 80 °C.

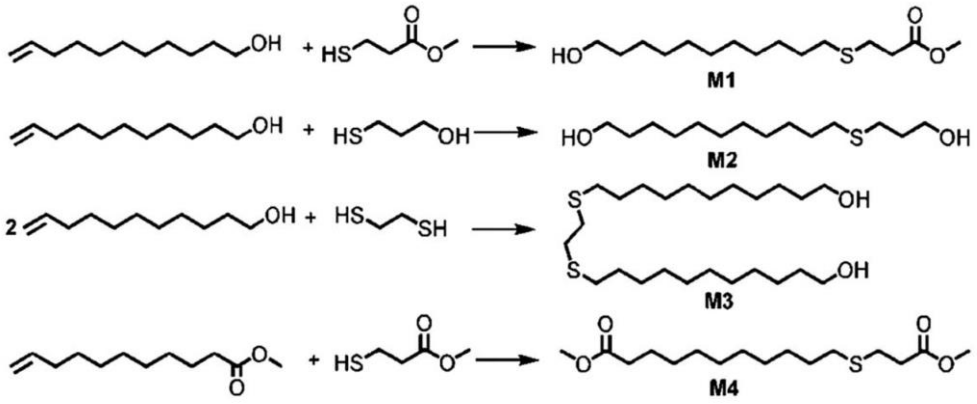
2.4. Sulphur-containing Polyamides

2.4.1 Thiol-ene Addition Reactions

Thiol-ene addition reactions are classified as click-chemistry reactions due to its simple processing, high yield, and none of by-products. However, it should be noted that the kinetics of thiol-ene reactions strongly depend on the structure of reactants, thiol and olefin compounds. Hoyle[38] claimed that the reactivity of 1-hexene is 8 times more than that of trans-2-hexene and 18 times more than that of trans-3-hexene. According to Hoyle[38], the reactivity of the ene compounds can be arranged as follows.

1. Norbornene > Vinyl ether > Propenyl > Alkene ≈ Vinyl ester > N-Vinyl amides > Allyl ether.
2. Allytriazine > N-Vinylamides > Allyether.
3. Allyltriazine ≈ Allylisocyanuratre > Acrylate > Unsaturated ester > N-substituted maleimide > Acrylonitrile ≈ Methacrylate > Styrene > Conjugated dienes.

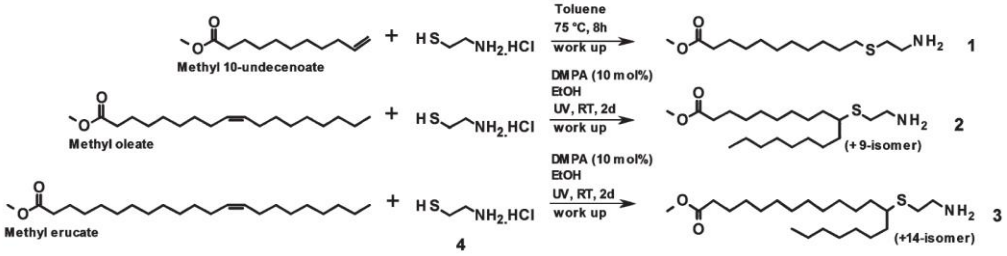
The thiol-ene reactions can easily proceed via a free radical initiator or UV light irradiated initiator mechanisms. Several radical thiol-ene addition reactions of fatty acid derivatives are showed in Scheme 4.



Scheme 4. The synthetic pathway to the new fatty acid derived polyester monomers[39]

2.4.2 Polyamides Synthesis via Thiol-ene Reactions

Plant oil derivatives are the important raw materials in oleochemical industry. Unsaturated fatty acids and their derivatives are common starting materials for polymers synthesis via thiol-ene additions. Turunc reported the synthesis of polyamides[39] by thiol-ene addition of cysteamine hydrochloride to the double bonds of from 10-undecenoate, methyl oleate, and methyl erucate. The monomers synthesis pathways were described in Scheme 5.



Scheme 5. *The synthesis pathway to fatty acid derived polyamide monomers.*[39]

All synthesized monomers were AB type for polyamidation, while, AABB type monomers have not been investigated yet. Our experiments were focused on AABB type monomer, diamines, synthesis which was first time explored for polyamide synthesis.

Part 2

Experimental Study

3. Experimental

A series of new saturated linear polyamides based on hexamethylenediame and long chain aliphatic carboxylic diacids have been synthesized via melt polycondensation reactions. Three polyamides, PA 6/14, PA 6/16 and PA 6/18 were synthesized from tetradecanedioic acid (C14), hexadecanedioic acid (C16) and octadecanedioic acid (C18), respectively. In addition, a fourth sulphur-containing polyamide was also synthesised via polycondensation, utilising a monomer prepared through thiol-ene click chemistry (Table 5).

Table 5. *Synthesized Polyamides and their monomers*

Polyamide	**Fatty Acid**	**Diamine**
PA 6/14	C14	Hexamethylenediamide
PA 6/16	C16	Hexamethylenediamide
PA 6/18	C18	Hexamethylenediamide
S-PA	10-Undecenoic Acid	Hexamethylenediamide

3.1. Materials

All reagents were used as received. Tetradecanedionic acid, hexadecanedionic acid, octadecanedionic acid were supplied by Neste. Hexamethylenediamide (HMDA), 1,2-ethanedithiol (EDT), 2,2-dimethoxy-2-phenylacetophenone (DMPA), 10-undecenoic acid (UDA), and acetonitrile were purchased from Aldrich. Ethanol was purchased from Altia. All other solvents were purchased from Aldrich.

3.2. Synthesis of long chain aliphatic polyamides

3.2.1. Nylon Salt Preparation

In general, fatty acids are insoluble in water, thus nylon salts were prepared in ethanol solvent. The nylon salt preparation procedure was applied to all polyamides in this study. Diacids were dissolved in absolute ethanol at approximately 70^0C to obtain 10 % clear transparent solutions. Then, 5 mole % excess of HMDA ethanoic solution was added dropwise to the stirring diacid solution across 20-30 min. The nylon salt precipitated as soon as it is formed, approximately after 10 min. After the addition was completed, the reaction mixture was continuously stirred for 30 min at 70^0C, following by 1 h at 0^0C (ice bath). The resulting product was filtered, and the precipitate was washed with ethanol. The product was dried in a vacuum oven overnight at 60^0C.

3.2.2. Melt Polycondensation

The polymerization process was conducted in a stainless steel reactor, following three steps. First, a particular amount of nylon salt was charged into the reactor. The temperature was increase gradually from room temperature to 30^0C above the salt's melting point (250 ^{o}C, 230 ^{o}C, and 220 ^{o}C, for PA 6/14, PA 6/16and PA 6/18, respectively) under a nitrogen purge. In second step, the nitrogen purge was stopped, all valves of the reactor were closed, and heating under pressure maintained for 2 h. Then nitrogen purge was applied again for 1 h to remove the major amount of water. Finally, medium-high vacuum (less than 0.07 mbar) was applied to remove the water by-product. The reaction time was longer than 24 h to archive sufficient molecular weight polymer. To harvest, the products were soaked immediately into liquid nitrogen to cool down and also prevent thermal degradation. The cooled products were collected by breaking off the whole sample into smaller specimens. The equipment used in polymerization is shown in Fig. 7.

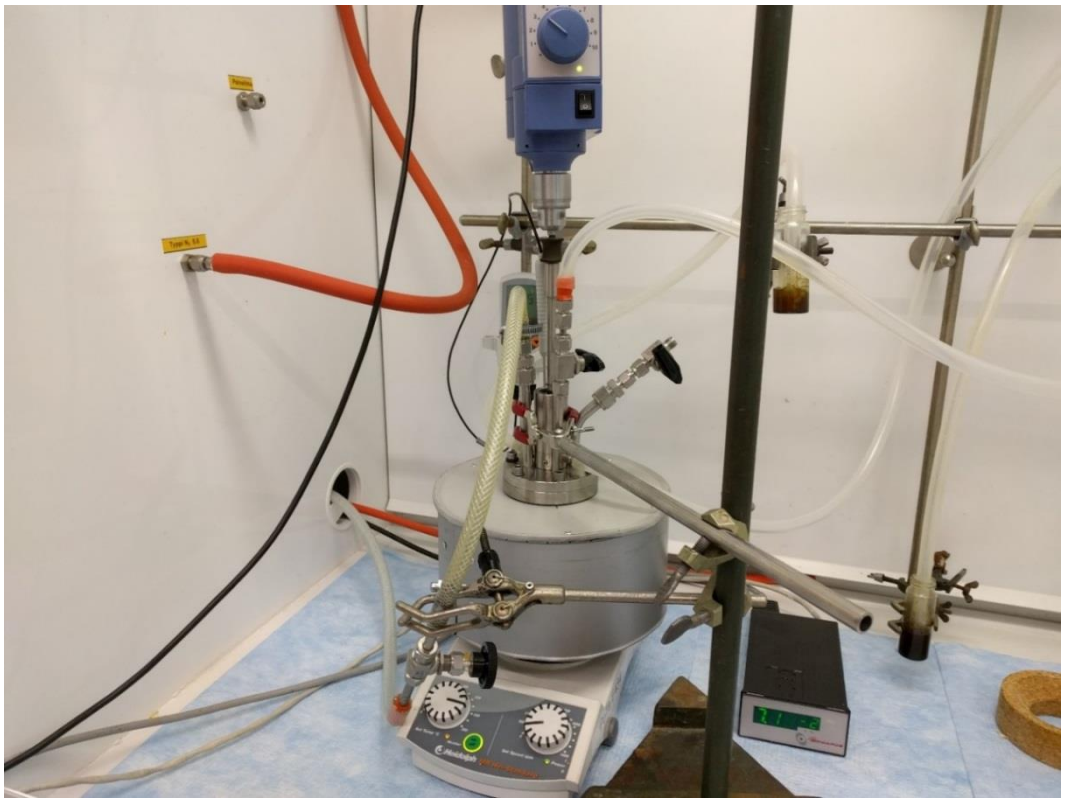
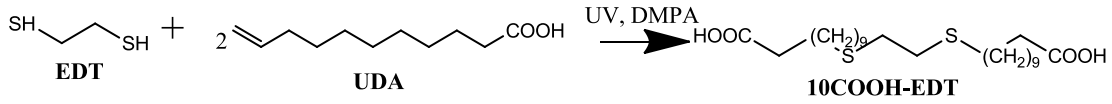


Figure 7. *Equipment and setup for melt polycondensation for polyamides*

3.3 Synthesis of sulphur-containing, long chain polyamides

3.3.1 Preparation of sulphur monomer via thiol-ene click chemistry

10-undecenoic acid and 1,2-ethanedithiol (molar ratio 2:1) were charged into a pre-dried bottle. In a separate beaker, DMPA photoinitiator, (1% mole of UDA) was dissolved in minimum amount of acetonitrile and added to the diacid/dithiol mixture. The whole mixture was entire covered with aluminum foil to prevent light radiation. The mixture was stirred with a vortex mixer overnight, then poured into Petri dishes. The reaction mixture was irradiated with a 15w lamp ($\lambda = 254$ nm) for 10 min. A white solid appeared, indicating the completion of the reaction. The product was purified by dissolving (at boiling point) and recrystallization from ethanol. Finally, the product was dried in a vacuum oven overnight at 60^0C. Scheme 6 describes the mechanism of this reaction.



Scheme 6. *Sulfur-contain di-carboxylic acid preparation*

3.3.2 Nylon salt preparation

The preparation of the nylon salt for the subsequent polycondensation of sulphur-containing polyamides was identical to that listed in Section 3.2.1 of this thesis.

3.3.3 Melt polycondensation

The polycondensation of sulphur-containing polyamides utilised the same procedure and equipment listed in Section 3.2.2 of this thesis, with the following variations:

- The melting temperature of the sulphur-containing nylon salt was 170 ^{o}C, thereby the reactor was heated to 200 C following the addition of the nylon salt.

3.3. Characterization of polyamides

3.3.1 Nuclear Magnetic Resonance

All proton Nuclear Magnetic Resonance (^{1}H NMR) measurements were conducted by Bruker AVANCE 400 MHz spectrometer at room temperature in deuterated chloroform with 10 v/v% of trifluoroacetic anhydride (TFFA). The co-solvent was used to poor solubility of long aliphatic chain polyamides in pure chloroform.

3.3.2 Thermal Analysis

3.3.2.1 Thermogravimetry (TGA)

Thermogravimetric Analysis (TGA) was performed using a TA Q500 Instruments. 5-10 mg of sample were heated at 10 ^{0}C/min from room temperature to 500 ^{0}C under a nitrogen atmosphere (flow rate: 40 mL/min).

3.3.2.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) analyses were conducted with a TA Q2000 Modulated Temperature DSC in order to observe the glass transition, crystallization and fusion processes. Nitrogen was used as the purge gas. Approximately 5 mg of sample were sealed in T-zero aluminum pans. The heating-cooling was programmed from 25-250 ^{o}C at 20 ^{o}C heating rate, with the samples being subjected to two heating-cooling cycles. The transition temperatures were measured the second heating/cooling cycle. All the measured temperatures were recorded at the peak values or middle-set values.

3.3.3 Mechanical Analysis

3.3.3.1 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) measurements were performed using TA Q800 DMA operating in tensile mode. A force rate of 3 N/min was applied on the sample specimens (films). Based on the plotted stress/strain curves, the Young's modulus of the samples were determined (the slopes of stress/strain curves). In addition to the Young's modulus, the glass transition temperatures were measured by DMA. The samples were heated from room temperature to 250 ^{0}C at 10 ^{0}C/min, while subjected to an 1 Hz frequency within a constant amplitude, 15 µm. The glass transition temperature are determined at the peak of Tan delta curve which is the ratio of the loss modulus and the storage modulus. Samples were analyzed in duplicate.

3.3.3.2 Tensile analysis (Instron Universal Tester)

Tensile analysis was conducted using an Instron 4204 Universal Tensile Tester with a 100 N static load cell. The film specimens were prepared in a rectangle shape, 5.3

x 20 mm^2 by press-cutting mold. The thickness varies in 0.1-0.3 mm range. The measurements were strain-control with strain-increasing rate 5 mm/min in humidity-controlled atmosphere, RH 50 %. Each measurement was repeated at least 5 times. The Young's modulus, yield stress, yield strain and, where possible, tensile strength and elongation at break were determined. Results presented are the average of five reproducible repeats.

3.3.4 Moisture Absorption

The water absorption content of polymers were measured by soaking a known-mass of polyamide were in distilled-water for 4 days. After this, the samples were taken out and excess water from the surface of the samples was dried gently by tissue paper. The water absorption percentages were calculated by the ratios of dry and their wet samples. Three specimens were measured for each sample.

3.3.5 Solubility

The synthesized polyamides were dissolve in ethanol, acetone, THF, DMSO, NMP,DMF, $CHCl_3$, formic acid, toluene, methanesulfuonic acid, m-cesol, hexafluoro propanol, dichloacetic acid, sulfuric acid and co-solvents such as formic acid/DCM (50:50 v/v %), and $CHCl_3$/TFFA (10:1 v/v %) at room temperature to determine solubility.

4. Results and Discussion

All polyamides were synthesized and characterized successfully at the lab-scale. The primary parameters regarding monomers synthesis and polymerization were evaluated. The potential limitations or requirements for processing and further up-scaling were identified.

4.1 Synthesis

4.1.1. Synthesis of Sulphur-containing Monomer

All aliphatic di-acids utilized in the synthesis of long chain polyamides (C14, C16, and C18) were used as received. However, in order to prepare sulphur-containing polyamides, a sulphur-functionalised diacid needed to be synthesized. This was achieved using a thiol-ene addition reaction between 10-undenoic acid and 1,2-ethanedithiol.

The synthesis process required only mild conditions; i.e. 70-80 ^{0}C temperature, glassware equipment, inner gases purge, atmospheric pressure and the reaction could be conducted in the presence of oxygen. Moreover, the reaction was accomplished rapidly (in less than 5 min), which indicates high reactivity of 10-undecenoic acid and ethylene dithiol in the UV irradiated thiol-ene reaction. The reactivity of the thiol-ene reaction depends significantly on the chemical composition of reactants. If there is any alternation of the position of the double bond in the diacid, or chemical structure of either the dithiol or alkene compounds, the reactivity can change significantly. Therefore, even a compound with a similar structure to 10-undenoic acid, 10-undecenoyl chloride, exhibited lower reactivity when subjected to the same thiol-ene reaction with 1,2-ethanedithiol . After the same reaction period, the product of the reaction involving 10-undeconoyl chloride remained in the liquid state with no sign of reaction, i.e. there were no solidified particles.

UV radiation with a photo initiator, DMPA, also plays an important role in this reaction, because neither high temperature (more than 70 ^{0}C) nor low temperature (less than -20 ^{0}C) at long reaction times (24 h) accelerated the rate of reaction. In contrast, a high conversion (up to and including 56.39 %) was achieved by UV radiation in a very short time (10 min). After purifying the product with several ethanol-washing cycles, the monomer did not contain unreacted dithiol or 10-undecenoic acid, nor any potential contaminants in the staring materials.

In order to optimize the sulfur-functionalized monomer preparation, the light radiation source, temperature range and initiator concentration must be further studied. Moreover, a sufficient production setup for a UV radiation reactor (batch or continuous line) is required to be designed for mass production. Besides, the sulfur-containing monomer was only synthesized from EDT, so other dithiol substance can be utilized in the monomer preparation process in further synthesis. The correlation between structure and properties should be determined.

4.1.2. Polymerization

4.1.2.1. Nylon Salt Preparation

Polyamide salts are essential intermediate feedstocks for polyamide polymerization since they guarantee a precise stoichiometric balance. This balance is required to obtain high molecular weight polyamides and prevent premature termination of the polycondensation reaction. In conventional Nylon 6/6 production, the stoichiometric balance is controlled by adjusting the concentration of HMDA monomer. The pH is maintained at a constant value (pH=7.6) by adding a particular amount of monomer to compensate for loss due to evaporation. The pH monitoring is required to be extremely accurate in order to calculate to exact amount of monomer input. The “perfect” stoichiometry balance seems to be difficult to be achieved using this pH monitoring method. Besides, a heavy-duty reactor design is required due to requirement of using a high pressure to prevent precipitation of the nylon salt. The reactors which can tolerate high pressure and temperature usually incur with high investment, operation, and maintenance costs.

Within the experiments presented in this thesis, using the ethanol dissolution/recrystallizing cycles, the excess monomer (diamine) and potential contaminants were completely removed by filtratation. Because both monomers have high solubility in ethanol solvent, especially diamine, they can be removed easily by filtration and washing of the filter cake containing nylon salt precipitate. Furthermore, during the conventional polycondensation process, the solvent was evaporated by boiling. This can't remove the excess monomers as well as any potential contaminants from either the raw materials or during the preparation process. The high purity of synthesized nylon salts were obtained when most potential contaminants substances were filtered off, providing a major advantage compared with the conventional 'evaporation process'.

The narrow molecular weight distribution is another essential improvement of this ethanol dissolution/recrystallization method. In the conventional polycondenzation, a specific amount of fresh monomers which can react either with the oligomers or monomers, were added into the nylon salt mixture. The reactions between the fresh monomers and oligomers were possible because the both monomers, and oligomers were always dissolved in the nylon salt solution by maintaining a high temperature and pressure throughout the nylon salt preparation process. Moreover, according to Odian[10], the reactivity of functional end-groups do not depend on the size of molecules, these reactions occurred randomly. Thus, the molecular weight distribution was expected to be broad. Within the syntheses presented in this thesis, the stoichiometry was controlled via nylon salt purification, as opposed to HDMA addition/compensation used during conventional polyamide production. When the Nylon salt were formed, they were precipitated immediately to prevent further reaction with monomers. Consequently, the molar mass distribution of nylon maintained narrow.

In the all experiments, nylon salt production was able to reach to high mass yield (> 92 %), indicative of the high efficiency of the process (Table 6).

Table 6. *The mass yields of nylon salts*

Nylon Salt	Yield (wt %)
PA 6/14	95.32
PA 6/16	97.84
PA 6/18	92.70
S-PA	96.08

Regarding environmental issues, water use is more favorable than ethanol as a solvent. Although all experiments were carried out in ethanol solution, an effective solvent recycling process can be applied straightforwardly to reduce the adverse impacts to the nature. Likewise, ethanol has a low boiling point (78 ^{0}C) so it's rather easy to evaporate completely from the nylon salts with a relative small amount of thermal energy. With an equal amount of ethanol, obviously water requires a larger amount of thermal energy to evaporate because of its higher boiling point (100 ^{0}C). Hence, the energy consumption within this novel ethanol dissolution/recrystallization process is expected to be considerably lower than the commercially-utilized water evaporation method. This is not only environmentally beneficially but also cost effective.

4.1.2.2 Polymerization

In the early stage of polycondensation, the water by-product was removed without any difficulty due to the low viscosity of the polymer melt. The viscosity increases along with reaction time at the same rate of the polymer growth, since the viscosity is proportional to molecular weight. When the polymerization reaction reaches a certain degree, the water molecules become trapped inside the melt. Therefore, the polymer melt must be agitated continuously and homogeneously to provide an efficient mixing and avoid "dead-spot" static regions. The mixing renews the melt's surface, which helps water molecules to move towards the surface layer. High vacuum also play an important role in assisting water evaporation. Due to the extremely high viscosity of the polymer melt, only water molecules on the melt's surface are able to evaporate. High vacuum creates the necessary driving force for

water molecules in the surface layer to detach from the melt. The applied low pressure also prevents the water molecules returning back into the polymer melt, which can degrade the polymer chains.

The polymerization was conducted using a small-size (150 mL), stainless-steel reactor which provided a sufficiently-high degree of variable/reaction control, but also displayed several difficulties in product harvesting and sufficient mixing of the molten polymer. The temperature was generated and controlled precisely by an electronic heating plate. High vacuum, less than 0.07 mbar, was able to be achieved in this reactor. However the vacuum pressure was not stable and fluctuated across a range of 0.2-0.07 mbar. Furthermore, the polymer melt was mixed by a propeller stirring rod which is more suitable for a dilute liquid, but does not adequately mix high-viscosity polymer melts, such as polyamides. Due to the spinning rotation of the stirring rod, the polymer melt tended to adhere around the rod. Additionally, due to the propeller shape at the end of the rod, the polymer products were difficult to detach and harvest. Due to these considerations, approximately 30-40 wt % amount of product was lost during the harvesting step.

There are several parameters to be taken into account if the synthesis would be scaled-up to the industrial production. The key principle is the efficiency of water by-product evaporation in order to obtain high molecular weight polymer. High vacuum and well mixing were essential factors to assist water vaporing and force the polymerization reaction to completion. Scale- up to industrial scale likely requires other reactor models, such as vented extruder reactors, to provide sufficient mixing, high vacuum pressure and temperature.

4.2. Characterization

4.2.1 Molecular Weight

The molecular weight of polymers and the degree of polymerization are some of the most important characteristics of a macromolecular material. As a general rule, higher average molecular weight polymers exhibit better mechanical and physical characteristics. Therefore, most polymer syntheses are required to meet a certain degree of polymerization for a particular application, especially in high-performance polymers. Commercial Nylons usually are produced within 10 000-34 00 g/mol molar mass which are relatively low compared to polyolefins.[14] However, due to the strong hydrogen bonding between amide groups, polyamides still display good mechanical properties, especially in fiber forms where the chains line in a highly oriented direction. Consequently, the degree of crystallinity increases due to the presence of amide linkages in the polymer chains. However, the crystallinity also depends on several different aspects such as processing conditions and thermal history, in addition to the chemical composition of polymer. Further discussion about the crystallinity of polyamide was displayed in Section 4.2.4.

Common analysis methods for determining macromolecular weight are Gel Permeation Chromatography (GPC), and viscometry. However, these measurements can only be evaluated if calibration was possible, and a sample displays a good solubility in a particular solvent. Suitable GPC columns were not available for measurement conditions. For molar mass measurement by viscometry, the constants of the Mark-Houwink equation for Nylon 6/6 are well-known, but these constants are not directly comparable to our synthesized polyamides because of large differences in the degree of amide groups. The average ratios of amide groups per carbon are 1:6, 1:10, 1:11, and 1:12 in Nylon 6/6, Nylon 6/14, Nylon 6/16, and Nylon 6/18, respectively. In this experiment, the average molecular weight was measured using proton (^{1}H) NMR analysis.

The NMR spectrum exhibit clearly end-group peaks and amide-group peaks which can be used to calculate the degree of polymerization. All proton NMR spectrum of

polyamides, excluding sulfur-containing polyamides, were displayed in a similar way. The ^{1}H spectra of PA 6/16 (30h) are shown in Fig. 8, peaks were found at 3.7 ppm (-NH-), 2.8 ppm (-CO-), and 2.6 ppm (end-groups –COO-).

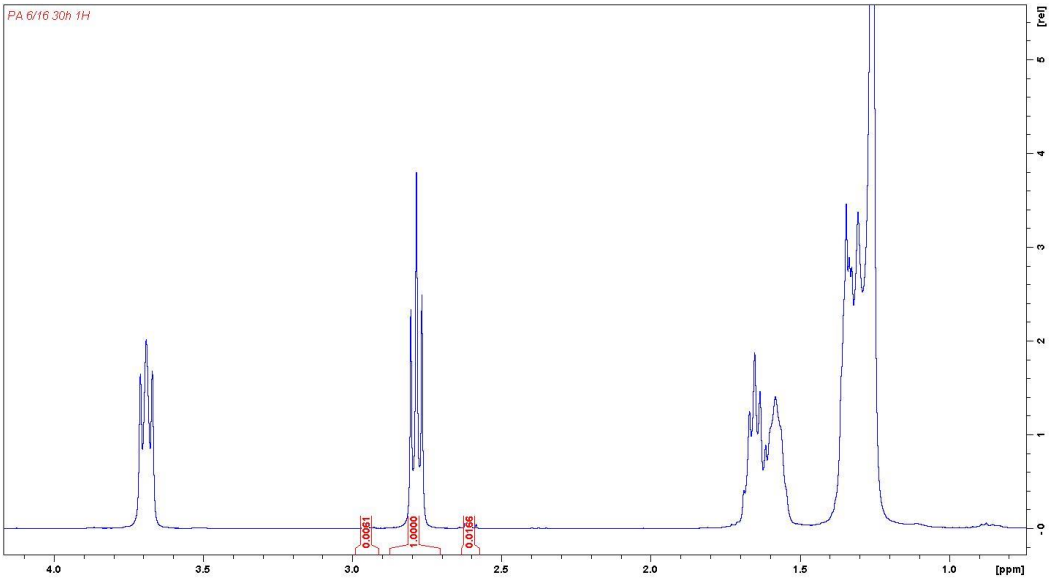


Figure 8. *NMR spectrum of Polyamide 6/16.*

The number-average molecular weight was calculated using Equations 1 and 2:

$$DP = \frac{CO/2}{COO/4} \quad (1)$$

$$M_n = DP \times mass\ of\ repeating\ unit \quad (2)$$

where DP is the degree of polymerizaiton, CO is the integral of the CO peak (at 2.8 ppm), COO is the integral of the carboxylic end-group peak (at 2.6 ppm) and M_n is the average number molecular weight.

Figure 9 describes the spectrum of S-PA. Beside amide peaks found at 3.7 ppm and 2.8 ppm, there are several peaks at 4.4 ppm, 3.05 ppm, 2.83 ppm, 2.74 ppm, and 2.58 ppm.

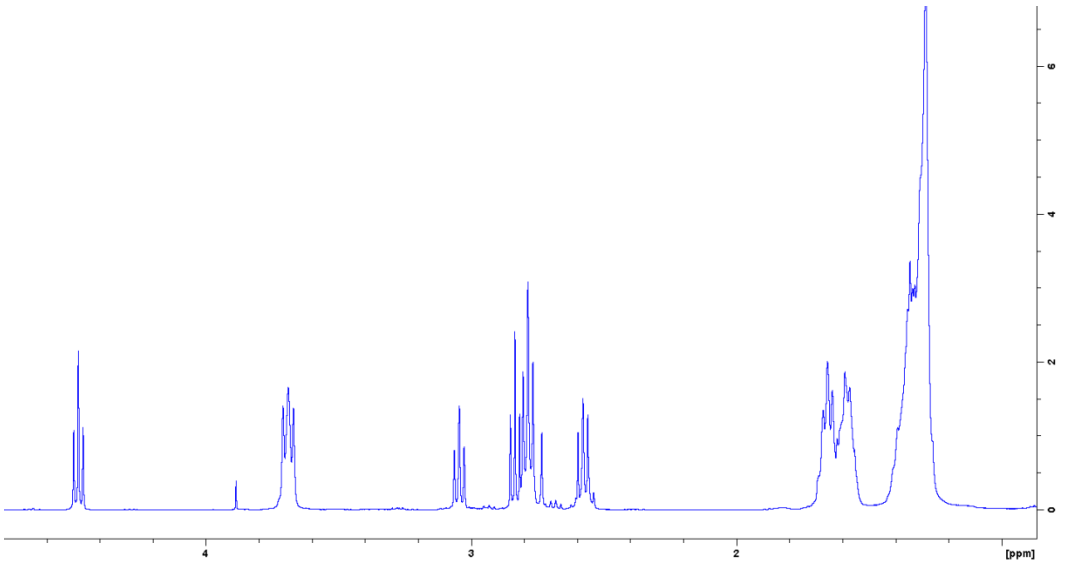


Figure 9. *H^1 NMR spectrum of S-PA*

Table 7 displays the average-number molecular weight of synthesized polyamides and commercial polyamides determined using NMR, along with other reference samples analyzed using other common methods for molecular weight determination. During polyamide production based on polycondensation, high molecular weight polymer chains are only synthesized during later stages of the polymerization. Hence the molecular weight is controlled by reaction time, and achieving high molecular weight polymers require a relative long reaction time. Compared with the commercial sample of PA 6/6 (M_n = 32 000 g/mol), the synthesized polyamides had significantly higher molecular weights up to 54 000, 48 000, and 37 000 g/mol for PA 6/14, PA 6/16, and PA 6/18, respectively. Table 5 displayed several synthesized commercial polyamides where the highest molecular weight was just above 35 000 g/mol (PA 10/11)[23] while all novel long chain synthesized polyamides had molar masses above 37 000 g/mol. Moreover, all synthesized polyamides have significantly higher molecular weight compared to the same type polyamides synthesized by the others. The higher molecular weights can be achieved when the reaction time were extended and by using the novel filtration method for nylon salt production, ensuring high monomer purity and precise stoichiometric control.

Table 7. *Molecular weight of synthesized polyamides and commercial references*

Polyamide	**M_n (g/mol)**	**Measurement Method**
References		
PA 6/14[18]	5 100	End-groups Titration
PA 6/18[25]	10 985	Viscosity
PA 6/18[20]	10 283	SEC
Commercial sample		
PA 6/6	32 000	NMR
PA 11	17 000	NMR
PA 12	30 000	NMR
PA 6/12	27 000	NMR
Synthesized PA		
PA 6/14 (8h)	18 000	NMR
PA 6/14 (24h)	54 000	NMR
PA 6/16 (15h)	20 000	NMR
PA 6/16 (24h)	49 000	NMR
PA 6/18 (24h)	37 000	NMR
S-PA	NA	NMR

The molecular weight growth is proportional to the reaction time; this was proved when the molecular weight of PA 6/14 increases from 18 000 g/mol to 54 000 g/mol for 8h and 24h reaction time, respectively. Similarly, the molecular weight of PA 6/16 increased from 20 000 g/mol to 49 000 g/mol for 15h and 24h reaction time, respectively. The reactions times for high molecular weight polyamides may be decreased, e.g. by using catalysts. In order to figure out the correlation between the polymerization time and the molecular weight growth, further experiments need to be carried out across a broader range of reaction time.

The size of aliphatic segment plays an essential role in defining the molecular weight. When the reaction times are equal, the molecular weights grow disproportionately to the segment's length. For instance, the molecular weight of PA 6/14, 6/16, 6/18 are 54 000, 48 000, 37 000 g/mol, respectively, for 24 h reaction time. One proposed reason for this behavior is the reduction in monomer reactivity with increasing chain length.

The molecular weight distribution, characterized by the polydispersity index (PDI), was not determined. The polydispersity would provide more insight of polymer properties because polymer properties are dominated by macromolecules rather than small molecules, i.e. monomers, oligomers, small molecules contaminants.[10]

The value of PDI can range between approximate 1.01 (very narrow molar mass distribution) up to more than 30, but in general it can be between 2 and 5. DSC exotherm and endotherm peaks provide an approximate indication on the molecular weight distribution of measured polyamides.

4.2.2 Crystallinity

The crystallinity degree of polymers is one of primary factor defining the characteristic of polymers such as physical, chemical properties, and especially the melting process which is dominated by crystalline regions. Highly crystalline polymers usually exhibit good mechanical properties, chemical resistance, barrier properties, and high reflective index due to their fine ordered structure. The correlation of the degree of amides and the crystallinity of polyamides should be further studied in the future. The degree of crystallinity of synthesized polyamides was as presented in Tab. 8

Table 8. *Degree of crystallinity of synthesized polyamides (24h reaction time).*

Polyamide	Degree of Crystallinity (%)
PA 6/14	24.5
PA 6/16	31.0
PA 6/18	30.4
S-PA	47.0

The sulfur-functionalized polyamide, S-PA, displayed an extraordinary high degree of crystallinity (47 %) which can be attributed to the presence of sulfur atoms along the main chain. Polymers can crystallize upon solvent evaporation, cooling from melt, or mechanical stretching. The crystallization starts from nucleation where polymer segments rearrange parallel in nano-sized areas. From nuclear, the crystals grow by further adding of folded polymer chain segments. Nucleation is strongly affected by foreign substances such as impurities, dyes, plasticizer, fillers, and other additives in the polymer networks. The presence of sulfur in the polyamides is suggested to assist the crystallization process, i.e. sulfur atoms playing a role as a nucleation site.

4.2.3 Thermal Analysis

Most of synthesized polymers are semi-crystal polymers which have both glass transition and melting point dominated by amorphous segments and crystalline segments, respectively. Good insight into the thermal behavior of polymers is necessary when considering application limits and processing conditions.

4.2.3.1 Glass Transition

The glass transitions were determined using DMA which is more sensitive at determining T_g determining than DSC.[40] Due to this lack of sensitivity, the glass transition temperatures were not visible in DSC curves for all synthetic polyamides.

Table 9 shows the glass transition temperature of several commercial polyamides and the synthesized long chain polyamides.

Table 9. *The glass transition of synthesized polyamides and commercial references.*

Polyamide	**T_g (ºC)**	**Carbon number/amide group**
Reference*		
PA 4/6	80	5
PA 6/6	46	6
PA 6	41	6
PA 6/10	42	8
PA 6/12	37	9
PA 11	42	11
PA 12	42	12
Synthesized Polyamides		
PA 6/14	71	10
PA 6/16	66	11
PA 6/18	67	12
S-PA	34	14

*reference values (Nylon Plastics Handbook)[14]

The decreasing trend of T_g was obviously corresponding to the enhancement of the methylene/amide ratio. S-PA exhibited the lowest T_g, 34 ºC, because its ratio was 14. Compared between AB type and AABB type polyamides with the same degree of amide groups, AABB polyamides tended to have higher T_g than AB type polyamides such as PA 6/6 vs PA 6 (46 ºC to 41 ºC); PA 6/16 vs PA 11 (66 ºC to 42 ºC), and PA 6/18 vs PA 12 (67 ºC to 42 ºC). The AABB polyamides generally contains a mixture of chains that have only amines, or only acid groups, while AB

polyamides has one amine and one carboxylic group at the end of each chain. The differences in the end group configuration can lead to essential differences in the morphology and characteristics of polyamides.[41]

4.2.3.2 Melting Points and Crystallization Temperature

The melting point, (T_m) and crystallinity temperature, (T_c) for novel polyamides synthesized compared to reference commercial polyamides are displayed in Table 10. All transition temperatures, measured by DSC, were determined from the second heating-cooling cycle in order to eliminate the effect of thermal history.

Table 10. *Thermal Characteristics of Synthesized Polyamides and commercial references*

Polyamide	**T_c (ºC)**	**T_m (ºC)**	**Carbon number/amide group**
Reference			
PA 4/6	-	295	5
PA 6/6	-	262	6
PA 6	-	220	6
PA 6/10	-	227	8
PA 6/12	-	218	9
PA 11	-	181,188	11
PA 12	-	178	12
Synthesized Polyamides			
PA 6/6	219	238, 259	6
PA 6/14	185	197, 207	10
PA 6/16	182	196, 201	11
PA 6/18	182	194, 200	12
S-PA	153	128, 169	15

Polyamides often possess two distinct melting endotherm, and this phenomenon was observed for all synthesized polyamides (PA 6/6 and PA 6/16 displayed unclear and overlapping multiple melting peaks in the second heating spectrum). The presence of two melting peaks are explained by the melting of two morphological regions, forms I and II. Form I is relatively fixed in the thermal process, while the form II melting temperature varies with annealing conditions and can either appear above or below Form I. Form I dominates the crystallization while form II is the recrystallization during heating.[33,42] Above glass transition temperature, the amorphous regions reach a maximum degree of flexibility, after which they will be transformed into crystallites which contribute towards the total crystallinity of the polymer. These recrystallization peaks are also observed in other semi-crystalline polymers such as polypropylene.[43] A typical DSC curve of polyamide, PA 6/14, was presented in Fig. 10.

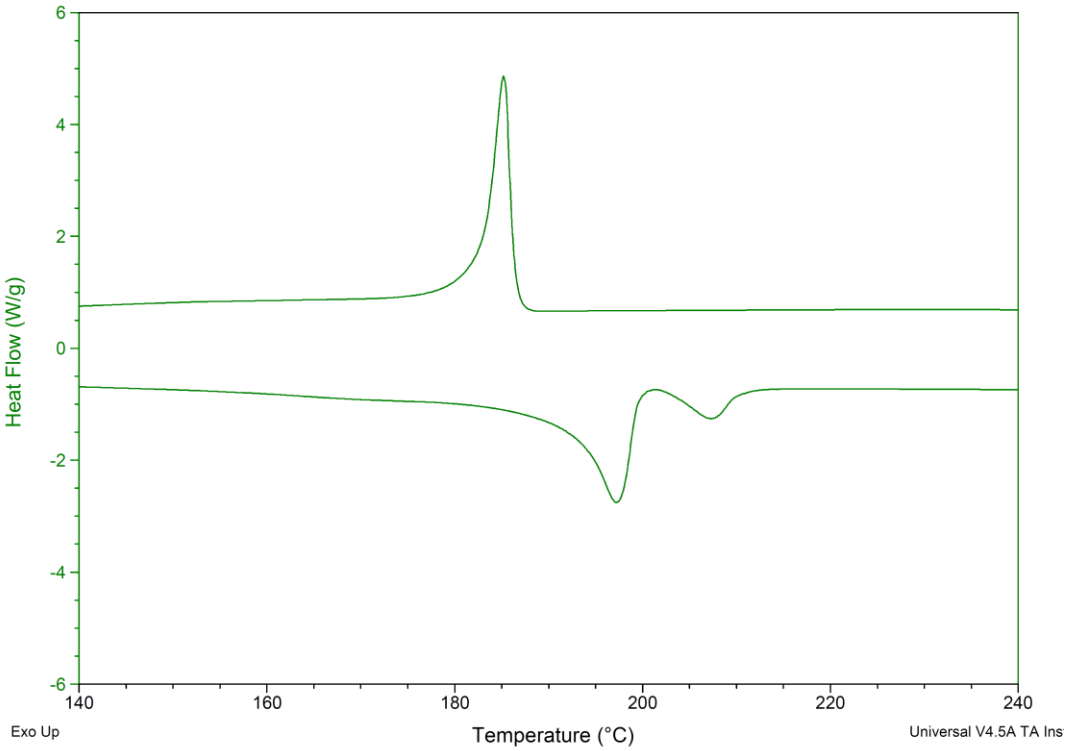


Figure 10. *DSC curves of PA 6/14*

The heat of fusion, the required thermal energy to melt the crystals, is always higher than the crystallization energy in all synthesized polyamides. This reveals that certain recrystallization occurs during the heating process, consequently, enhancing

the total crystallinity of the polymers. The XRD measurements reveal that the crystallinity of synthesized polyamides are 24.5 %, 31.0 %, 30.4 %, and 47 % for PA 6/14, PA 6/16, PA 6/18 and S-PA, respectively, which also fit along to the crystallization energy measured by DSC. Although there are minor differences in chemical composition between our polyamides, their crystallinity can be estimated by the crystallization energy. PA 6/16 and PA 6/18 have similar degree of crystallinity, measured by XDR, consequently their crystallization energies are also approximately equal, 53.15 J/g and 54.47 J/g, respectively (Table 11).

Table 11. *Thermal fusion and crystallization energy of synthesized polyamides*

Polyamide	**Crystallization (J/g)**	**Fusion (J/g)**
PA 6/6	53.17	62.63
PA 6/14	43.35	65.85
PA 6/16	53.15	70.58
PA 6/18	54.47	73.30
S-PA	68.72	78.90

Another remarkable phenomenon observed from DSC curves is the sharp crystallinity exotherm peaks which indicate the crystallites were formed homogeneously and the size distribution of crystallites was narrow. The uniform crystallites also indicate that the molecular weights of polymers are relatively homogenous and the PDI is narrow (Fig. 11).

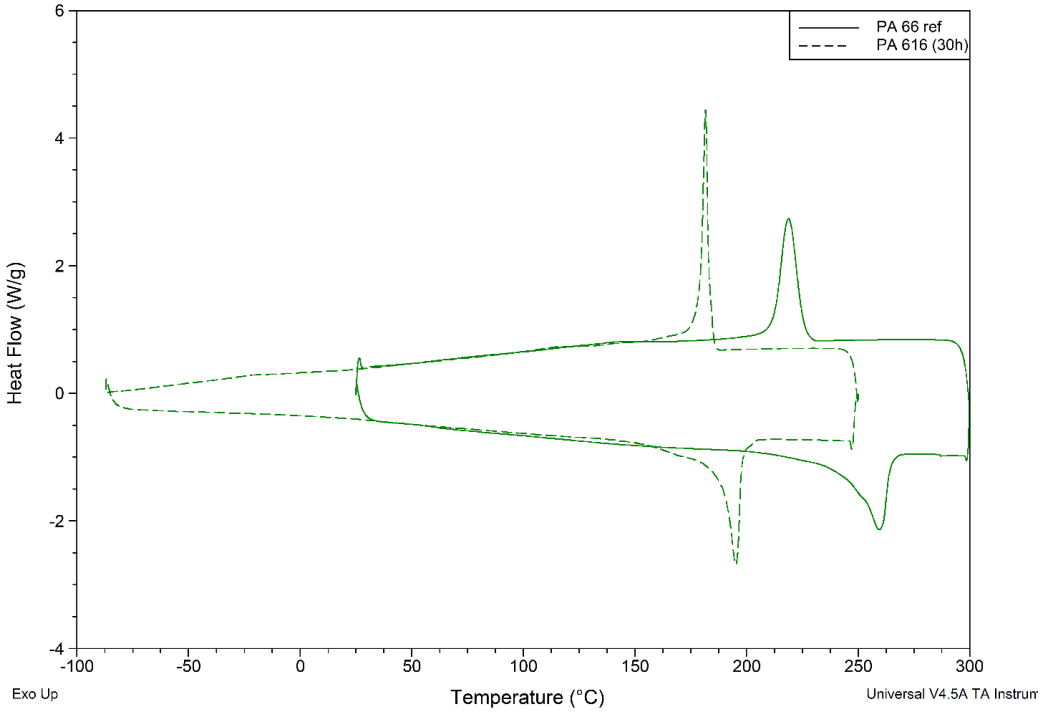


Figure 11. *DSC curves of PA 6/6 and PA 6/16*

The synthetic polyamides were all composed of long chain diacids but with different aliphatic segment lengths, excluding the sulfur-functionalized polyamide. Based on the chemical composition, obviously, longer aliphatic segment monomers have a lower degree of amide groups which is the key parameter defining the properties of polyamides. The high amide group containing polyamides exhibited stronger bonding between polymer chains. The DSC data indicated a decrease in T_m regarding to the increase in the aliphatic content of diacid units. The longer aliphatic segment polyamides have lower melting points, especially sulfur-containing polyamide S-PA (T_m = 169 ^{0}C), its monomers contain 24 carbons. However low melting point is also an advantage in processing when less energy is required.

4.2.3.3 Degradation Temperatures

Thermal stability properties of synthesized polyamides were measured by TGA in a nitrogen atmosphere. Generally the thermal stability of all synthesized polyamides were determined as good level. The decomposition temperatures were indicated at

491 ^{0}C and 432 ^{0}C for non-sulfur and sulfur-containing polyamides, respectively (Fig. 12 and Table 12). Compared with commercial PA 6/6, these novel polyamides were had slightly better thermal stability, excluding S-PA. In Fig. 12, the derivative of weight curves of novel polyamides were narrower than the commercial PA 6/6, which indicate the high homogeneity in their size distribution. On the other hand, S-PA performed lower and had broad thermal degradation range which started degrading from 350ºC to 500ºC. The full explanation needs further studies.

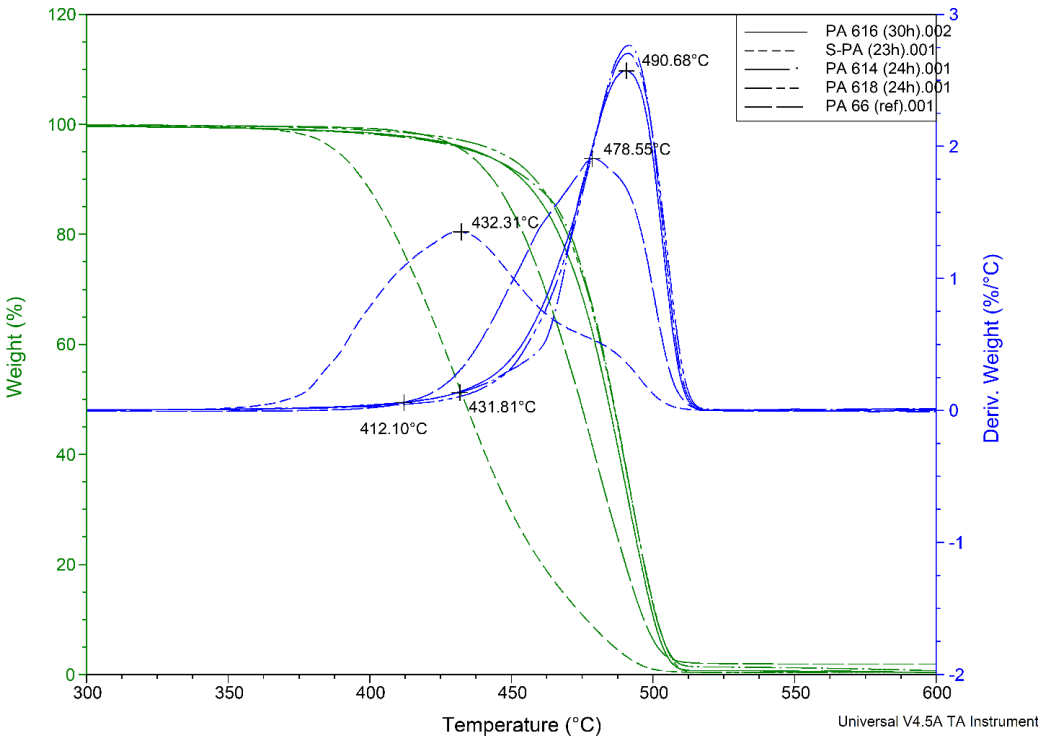


Figure 12. *TGA curves of synthesized polyamides*

Table 12. *The degradation temperature of synthesized polyamides.*

Polyamide	**T_d (ºC)**	**Carbon number/Amide group**
PA 6/6	479	6
PA 6/14	491	10
PA 6/16	491	11
PA 6/18	491	12
S-PA	432	14

4.2.4 Mechanical Properties

The mechanical properties were determined at room temperature using an Instron tensile testing device, and at selected temperatures (30 ^{o}C, 70 ^{o}C, and 100 ^{o}C) by dynamic mechanical analysis.

4.2.4.1 Tensile Test

Dry, melted-pressed polyamides films were prepared and their mechanical properties were measured under standard tensile testing conditions at room temperature. Generally, according to the reference values and our measured data, the strengths of polyamides were reduced when the aliphatic segment's length increased. The Young's moduli of measured samples were found to be in range of 450-1150 MPa for entire series; the tensile strength were between 32 and 45 MPa (Table 13). Compared with the most common PA 6 and PA 6/6, the mechanical properties of our polyamides were measured as lower strength, their Young's modulus being approximately 1/3 of either PA 6 or PA 6/6. The novel synthesized polyamides displayed Young's modulus, tensile strength and tensile yield strength values that were comparable with commercial PA 11 and PA 12 (both having similar amide degrees as the synthesized polymers).However, the elongation at break of novel polyamides synthesized were found to be much higher, within the range of 320-600 %. In addition, the elongation at yield, the degree of deformation when they still can full-recovery, were found as excellent performance (21-26 %). However, the sulfur-containing polyamide showed relatively low mechanical strength with 450 MPa Young's modulus and 32 MPa tensile strength. The explanation for low mechanical properties of S-PA may connect to its high methylene/amide ratio.

Table 13. *Tensile Test Results of synthesized polyamides analysed using the Instron tensile testing device, and values of commercial reference polyamides*

PA	Young's Modulus (MPa)	Yield Strength (MPa)	Tensile Strength (MPa)	Yield Strain (%)	Break Strain (%)
Reference*					
PA 4/6	3000	79	99	NA	30
PA 6/6	3200	83	83	5	60
PA 6	3000	81	81	9	150
PA 6/9	1900	70	NA	10	50
PA 6/10	2400	59	59	10	100
PA 6/12	2100	61	61	7	150
PA 11	1360	36	59	22	330
PA 12	1500	52	55	10	250
Novel PA					
PA 6/14	1150	44	45	21	400
PA 6/16	1010	44	43	22	320
PA 6/18	1010	42	44	26	490
S-PA	450	29	32	26	600

*reference values (Nylon Plastics Handbook)[14]

4.2.4.2 Dynamic Mechanical Analysis

The tensile tests were conducted by DMA measurement at selected temperatures (30, 70 and 100 °C) to determine the tensile properties of the novel polyamides under practical working environments and conditions. The Young's moduli values are summarized in Table 16. At approximately room temperature, 30 ^{0}C, most of the polyamides exhibited a good hardness while Young's Modulus were measured above 1 GPa which nearly equal to polypropylene[44]. When the temperature increased above T_g, (70 ^{0}C), the Young's Modulus reduced by approximately half to 500 MPa. At 100 ^{0}C, much higher than T_g, the Young's Modulus still remained

around 240-300 MPa (Tab. 14). As conclusion from these measurements, the synthesized polyamides remained good mechanical properties even above softening temperature, T_g.

Table 14. *Young's Modulus of synthesized polyamides at 30 ^{0}C, 70 ^{0}C and 100 ^{0}C*

	Young's Modulus (MPa)		
	30 ^{0}C	**70 ^{0}C**	**100 ^{0}C**
PA 6/14	1 162	533	238
PA 6/16	1392	543	388
PA 6/18	1 224	555	294
S-PA	799	341	224

Moreover, above T_g, the mobility of polymer chains enhances, which provides sufficient energy for recrystallization. Stress-strain curves of PA 6/16 provide a typical example, as shown in Fig. 13. At 70 ^{0}C and 100 ^{0}C, the stress continuously increases at a higher rate after the yield point, i.e. strain hardening phenomenon. This indicates increased toughness within the materials, and a tendency to undergo ductile- rather than brittle deformation, due to the suppression of strain localization.[45] However, because the maximum applied force of DMA is limited to 18 N, the tensile strength and elongation at break were not able to be measured using DMA.

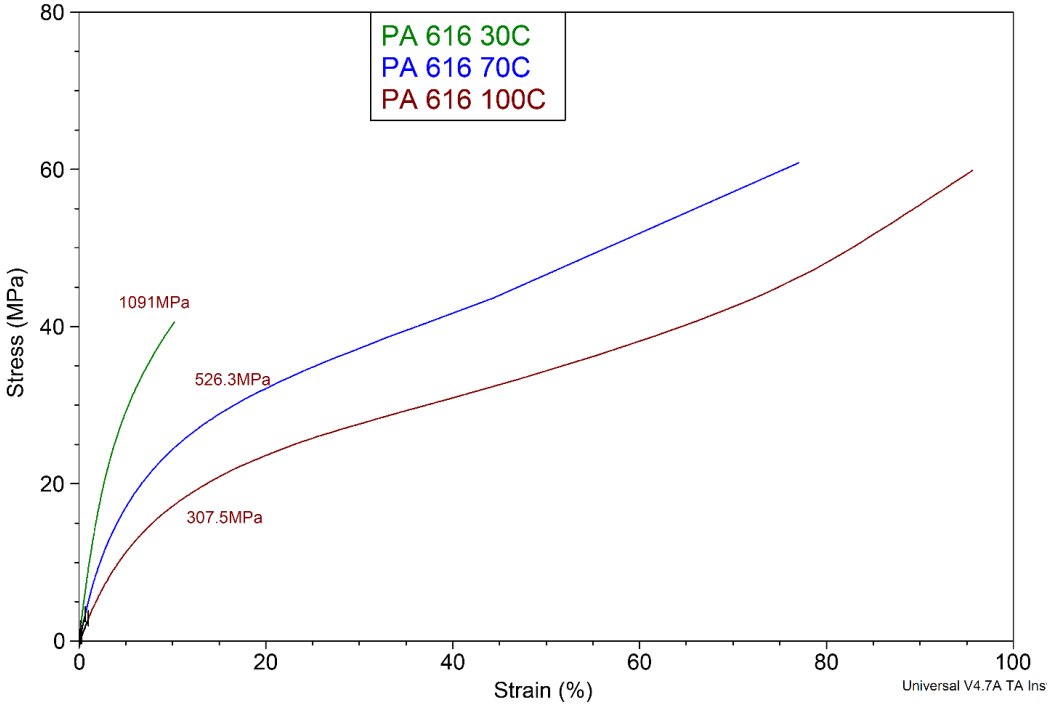


Figure 13. *Stress-strain curves of PA 6/16 at 30 ^{0}C, 70 ^{0}C and 100 ^{0}C*

4.2.5 Moisture Absorption

Due to amide linkages, polyamides undergo hydrogen bonding not only between polymer chains but also with water molecules in the surrounding environment. The property of moisture absorption of polyamides is a challenge for processing, storing and extended use. Moisture is known to affect polymer characteristics such as dimensional stability, mechanical, chemical and physical properties. Adsorbed moisture within polyamides acts as a plasticizing agent that reduces the interaction bonding and entanglement between polymer chains. This results in an increase in 'free' (unoccupied) volume and chain mobility.

The moisture absorption ability of polyamides depend on the density of amide linkages on the polymer chain. A smaller number of amide linkages leads to reduced moisture attraction. Compared with commercial PA 6/6, the long aliphatic segments polyamides PA 6/14, PA 6/16, PA 6/18 and S-PA have remarkably less moisture absorption ability, 7.64 % to 2.9 %, 1.23 % 0.84 % and 0.79 %, respectively (Table

15). Sulfur-containing S-PA has the best anti-moisture absorption ability and also the lowest degree of amide linkages. Moreover, an increase in polymer chain length (molecular weight) also leads to better moisture resistance- as indicated by the water absorption decreasing with increasing reaction time/higher molecular weight. For example, the moisture absorption of PA 6/16 reduced from 1.77 % to 1.57 % and 1.23 % with 15 h, 24h, and 30 h reaction time, respectively (Table 15).

Table 15. *Moisture Absorption of Synthesized Polyamides and commercial references*

Polyamide	**Water Absorption (%)**
Reference*	
PA 4/6	15.00
PA 6/6	8.50
PA 6	9.50
PA 6/9	4.50-5.00
PA 6/10	3.30
PA 6/12	3.00
PA 11	1.90
PA 12	1.60
Novel Polyamides	
PA 6/6 (reference)	7.64
PA 6/14 (24h)	2.90
PA 6/16 (15h)	1.77
PA 6/16 (24h)	1.57
PA 6/18 (24h)	0.84
S-PA (23h)	0.79

* Measured at 100 % RH. Source: Nylon Plastics Handbook[14]

4.2.6 Solubility

The chemical resistance of the novel long chain polyamides was determined by the solubility in a wide range of solvents (Table 16). Methanesulfonic acid, m-cresol, hexafluoro-2-propanol (HFIP), and co-solvent $CHCl_3$/TFFA proved to be good room-temperature solvents for all synthetic polyamides. The novel long chain polyamides displayed similar solubility properties as their commercial, shorter-chain equivalents. One main difference was the increased resistance to formic acid displayed by all novel polyamides, while C18 displayed further resistance to the formic acid/DCM solution. The sulfur-containing polyamide exhibited the best chemical resistance property, with the concentrated sulfuric acid (95-97 %), dichloacetic acid and co-solvent formic acid/DCM failing to dissolve S-PA at ambient temperature. Immersing the sulphur-containing polyamide in dichloacetic acid resulted in the only example of gel-formation observed. The amide groups not only form the hydrogen bonding with each other, but also with solvent molecules in solution. Therefore, high degree of amide group results in poor chemical resistance. Compared with other novel polyamides, S-PA has the highest methylene/amide ratio (10, 11, 12 and 14 for PA 6/14, PA 6/16, PA 6/18 and S-PA, respectively), which assist S-PA performed better resistance to chemical than the others.

Table 16. *Solubility of polyamides in various solvents. Polymers marked with an asterisk are commercially-obtained polyamides, all others were synthesised.*

Polyamide	**6/6***	**12***	**6/12***	**6/14**	**6/16**	**6/18**	**S-PA**
THF	-	-	-	-	-	-	-
DMF	-	-	-	-	-	-	-
$CHCl_3$	-	-	-	-	-	-	-
NMP	-	-	-	-	-	-	-
Formic Acid	+	-	+	-	-	-	-
DMSO	-	-	-	-	-	-	-
$CHCl_3$/TFFA	+	+	+	+	+	+	+
Methanesulfonic Acid	+	+	+	+	+	+	+
Formic Acid/DCM	+	+	+	+	+	-	-
H_2SO_4	+	+	+	+	+	+	-
m-Cresol	+	+	+	+	+	+	+
Dichloacetic acid	+	+	+	+	+	+	**G**
HFIP	+	+	+	+	+	+	+

+: dissolvable, –: not dissolvable, G: gelation

5. Conclusions

Long chain aliphatic polyamides (PA 6/14, 6/16 and 6/18) were successfully synthesized via polycondensation, using long-chain aliphatic dicarboxylic acids (namely, tetradecanedioic acid (C14), hexadecanedioic acid (C16), octadecanedioic acid (C18)). Synthesis was conducted at bench-scale (approx. 150 mL reactor), with reaction times varying from 15 to 24 h. Several factors were crucial for the successful synthesis of high molecular weight polyamides. These factors include:

- An oxygen-free environment to prevent degradation of the polymer due to oxidation
- Sufficiently high vacuum (less 0.1 mini bar)to assist in water by-product removal during polymerization
- Sufficiently low pressure to prevent water re-adsorbing onto the surface of the polymer melt
- Sufficiently high stirring (shear) to encourage an even and homogenous polymer mixture during the polymerization process, and to allow water to migrate through the melt to the surface, and eventually evaporate.

In addition to the aforementioned factors, arguably the most crucial for successful polymerization is a precise stoichiometric ratio between diacid and diamine. A novel nylon salt preparation process was developed which involved dissolution and recrystallization in ethanol prior to being added into the reactor as a dry powder. This is in contrast to conventional polyamide polymerization techniques, which utilize a water solution of nylon salt that is subsequently heated, with additional diamine being added to compensate for the stoichiometric unbalance. Compared with conventional method, the novel nylon salt preparation process developed in this work has three main advantages;

1. high purity due to limitation of exceed monomer and potential contaminants during the dissolution/recrystallization cycles
2. excellent stoichiometry control by purification
3. homogeneous size distribution of the final product.

Consequently, the novel nylon salt method resulted in high molecular weight polyamides (up to 54 000 g/mol as measured with NMR These high molecular weights are possible without utilising solid-state polymerisation, providing a clear benefit over conventional polyamide processing techniques.

In addition to the long chain polyamides, a novel sulphur-containing polyamide was also synthesised utilising the same polycondensation method. Prior to polymerisation, the sulphur-functionalised diacid was prepared by reacting 10-undecinoic acid (a castor oil derivative) and 1,2-ethanedithiol via a thiol-ene addition reaction. The resulting functionalised monomer was easily synthesised using UV light, resulting in high yield and purity. Furthermore, the monomer was a very long sulfur-containing monomer (24 carbons) for polyamide synthesis. This is the first 24-carbon aliphatic sulphur containing diacid monomer for polyamidation reported.

The novel synthesized polyamides were characterized and compared with different commercial products; PA 6, PA 6/6, PA 6/12, PA 11, and PA 12. Properties were primarily influenced by the length of the diacid aliphatic segment and the ratio of carbon:amide groups. As mentioned previously, the novel long chain polyamides showed high molecular weights and good homogenous molecular weight distributions. The highest molecular weight values were achieved at longer reaction times and in polyamides containing diacids with shorter aliphatic segments (ie. C14). The solubility/chemical resistance of the long chain polyamides was comparable with their commercial products for a range of solvents, except that they were insoluble to also to formic acid ; the sulphur-containing polyamide displayed the greatest resistance to dissolution being insoluble also to sulphuric acid.

The degree of crystallinity of the long chain polyamides ranged from 25-30 %, with the DSC spectra displaying sharp crystallization peaks; this indicates a narrow size distribution of crystallites. The sulphur-containing polyamide displayed a higher degree of crystallinity of 47 %, possibly attributed to sulphur acting as a nucleating agent. The novel polyamides displayed comparable tensile properties as commercial equivalents, while also displaying enhanced elongation/ductility and dimensional stability at temperatures above the $T_{g.}$ Superior moisture barrier

properties were displayed by the long chain polyamides, with water repulsion enhancing with longer chain length and a reduction in the total number of amide groups in the polymer. Sulphur-containing polyamides yielded the lowest water absorption values.

The novel, long chain polyamides were readily synthesized utilizing a modified conventional polycondensation technique that could be readily up-scaled. Furthermore, this modified polymerization process yielded polyamides which displayed properties superior or comparable to conventional commercially-available polyamides. Thus, the novel polyamides possess great potential for a range of applications.

There exists a great potential for future research regarding the synthesis and properties of long chain polyamides derived from renewable sources. These include:

- The use of other suitable renewable derivatives (diacids of varying aliphatic chain length) in the polycondensation reaction
- Optimization of the sulfur-functionalized monomer preparation process, including the light radiation source, temperature range and initiator concentration
- Reactor and process design for potential upscaling of the synthesis process
- Further in-depth property analysis and structure-property correlations, including:
    - Molecular weight determination via SEC/GPC
    - The influence of amide group density on crystallinity
    - Rheological properties of molten polyamides
    - Environmental (UV, water, solvent, etc.) stability studies
    - Blending trials with polyolefins. The longer chain polyamides are expected to reduce the polarity of polyamides, encouraging miscibility with polyolefins and eliminating the need for compatibilizers

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